INTRODUCTORY
CHEMISTRY

(PHYSICAL)
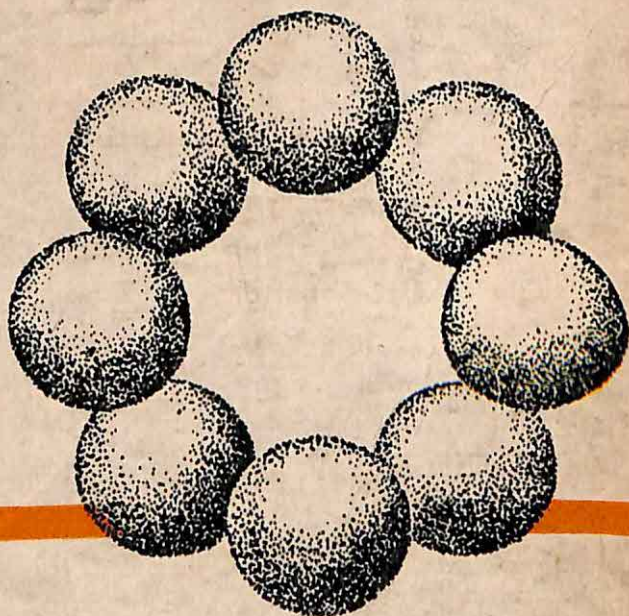
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BHARATI
BHAWAN
(P&D)

Introductory Chemistry

(Part I—Physical Chemistry)

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PREFACE

For the past few years, the necessity of a suitable book on Chemistry for the intermediate students covering the syllabi as well as the requirements for various competitive examinations has been haunting my mind. The present book **Introductory Chemistry** is an endeavour in that direction. This book is primarily designed to serve as a textbook for the 12th class of the 10+2 system.

The style of presentation is simple, arrangement of topics is systematic and the sequence of facts have been tried to be made as smooth as possible. Considerable stress has been given to explain the fundamental principles in the light of modern trends in chemical thought.

The special features of the book are—

(i) It contains a large number of schematic diagrams and data to enable the students to understand the subject clearly.

(ii) A large number of patent questions with answers have been given so as to make a visual impact on the young mind.

(iii) It includes a varied pattern of questions and problems required for the competitive examinations.

(iv) A large number of exercises have been given to provide an opportunity to the students to answer them.

(v) Objective type questions with answers at the end of each chapter have been preferably dealt with as they are becoming increasingly important.

In the concluding portion of the book a number of miscellaneous questions with appropriate answers have been included in a separate chapter.

Appendices provided are relevant and in tune with the essential requirements of class XII students.

The author expresses his deep sense of gratitude to all those who extended help in any form in the preparation of the manuscript.

The author records his indebtedness to the publisher Bharati Bhawan (Publishers & Distributors) as well as to the staff Tapan Printing Press, Patna for courtesy and co-operation in bringing the book to his satisfaction.

Suggestions for improvement and better methods of presentation in the book will be thankfully acknowledged.

AUTHOR

CONTENTS

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ATOMIC STRUCTURE

It was speculatively conceived in the works of ancient Greek philosophers Leucippus, Democritus, Epicurus and others that atoms are the smallest indivisible particles, of which all substances are built up.

However, the development of the atomic concept of matter was due to the works of Dalton who firmly advocated the **indivisible nature of atom**.

But now-a-days studies on radio-activity, electrical discharge in gases, electrolysis and other phenomena have conclusively shown that atom has a definite structure and that it can be further sub-divided into still smaller fragments. Experiments have shown that an atom contains electrons, protons and neutrons.

The Discovery of Electrons (Cathode rays) :

Cathode rays were discovered by Julius Plucker in 1859 and latter studied exhaustively by J. J. Thomson in 1897. It was found that the passage of electricity in a discharge tube using a gas under a pressure as low as 0·01 mm of mercury produced a stream of rays from the cathode. These rays are known as the **Cathode rays**.

Properties of Cathode rays : (i) The cathode rays travel in straight lines and cast shadows of objects placed in their path.

(ii) They are emitted at right angles from the surface of the cathode.

(iii) When they fall on certain substances, they produce fluorescence, the colour depending on the nature of the substance.

(iv) When they fall on an obstacle, the temperature of the latter is raised appreciably.

(v) They can pass through thin sheets of matter without puncturing it. They can pass through few cms of air.

(vi) They ionise the gas through which they pass.

(vii) They travel with velocity ranging from 1/3 to 1/10 of that of light.

(viii) When they fall on a heavy solid substance (anti-cathode) like platinum and tungsten, they produce highly penetrating invisible rays, called **X-rays** or **Roentgen rays**.

(ix) The cathode rays cause mechanical effect in a small paddle wheel placed in their path. This shows that cathode rays consist of material particles.

(x) These rays are deflected in an electric or magnetic field from their normal path in a direction indicating that they are negatively charged particles.

The negatively charged particles constituting the cathode rays are called electrons which are formed by the disintegration of atoms of the gas under high electrical tension or from the material of the cathode itself. The electrons were found to possess the same properties, irrespective of the material of the electrodes or the nature of the gas in the discharge tube.

Mass of an Electron :

The charge to mass ratio *(e/m)* of an electron was measured to be $1 \cdot 759 \times 10^7$ e.m.u./gm. The value of e/m_H for hydrogen atom is $0 \cdot 9577 \times 10^4$ e.m.u./gm. Hence,

$$\frac{\text{mass of the electron}}{\text{mass of the } H\text{-atom}} = \frac{m}{m_H} = \frac{0 \cdot 9577 \times 10^4}{1 \cdot 759 \times 10^7} = \frac{1}{1840}$$

i.e., the mass of an electron is smaller than that of hydrogen atom in the ratio 1 : 1840.

The Discovery of Protons (Positive rays) :

Goldstein in 1886 observed the presence of another type of rays in the discharge tube. These rays are known as **positive rays** or **Canal rays**. The positive rays are found to possess the following characteristics :

(i) These rays flow from the direction of the anode towards the cathode.

(ii) They are found to deflect in an electric field or a magnetic field in the direction showing that they are positively charged material particles.

Experiments have shown that the charge to mass ratio *(e/m)* of such a particle depends upon the nature of the gas in the discharge tube. The value of this ratio is found to be minimum for hydrogen, i.e., 10^5 coulombs/gm. Such particles in case of hydrogen are called protons.

Origin of positive rays : On the application of a high voltage through the discharge tube, electrons are ejected from the cathode. These electrons move towards the anode and on their way they collide with the gaseous molecules. The electrons being very energetic cause the removal of electron from the molecules of gas.

$$
\begin{aligned}
H_2 &\rightarrow H + H \\
H &\rightarrow H^+ + e \\
H_2 &\rightarrow H_2^+ + e
\end{aligned}
\left.\right\}
$$

$$\left.\begin{array}{l} O_2 \rightarrow O \quad +O \\ O \rightarrow O^+ \quad +e \\ O_2 \rightarrow O_2^+ \quad +e \\ O_2^+ \rightarrow O_2^{++} +e \end{array}\right\}$$
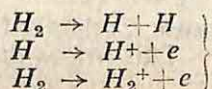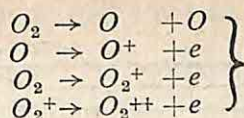
The gaseous ions thus formed travel towards the cathode. The rays constituted by positive H^+ ions are known as **protons**.

Neutron :

James Chadwick in 1932 obtained a new radiation from the bombardment of beryllium ($_4Be^9$) with α-particles.

$$_4Be^9 + _2He^4 \rightarrow _6C^{12} + _0n^1$$
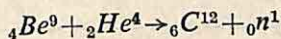
This new radiation was found to consist of particles having no charge. The mass of the particle was almost equal to that of proton. This particle was named **neutron** because of its electrically neutral character.

The three particles electron, proton and neutron are called **fundamental particles**.

Charge and Mass of Fundamental Particles

Particle	Mass		Charge	
	Relative	Absolute	Relative	Absolute
Electron	0·000544 amu ≈ 0	$9·1083 \times 10^{-28}g$	-1	$4·80216 \times 10^{-10}$ e.s.u. or $1·60206 \times 10^{-19}$ coulomb
Proton	1·0073 amu ≈ 1	$1·6735 \times 10^{-24}g$	$+1$	$4·80216 \times 10^{-10}$ e.s.u. or $1·60206 \times 10^{-19}$ coulomb
Neutron	1·0086 amu ≈ 1	$1·6747 \times 10^{-24}g$	0	0

Rutherford's α-scattering experiment :

In 1904, Rutherford observed that if α-particles are allowed to impinge on a thin gold foil, most of the α-particles passed through the foil without any deviation, some were deflected from the path
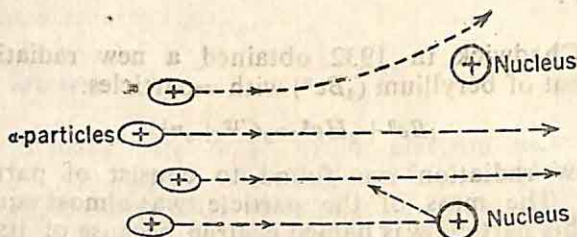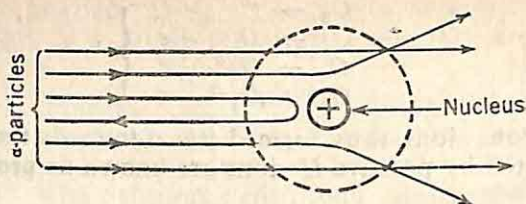
whereas a very few were found to be reflected back. These observations led Rutherford to put forward his **nuclear theory of atom.** According to this theory—

(i) Most of the space in the atom is empty.

(ii) Most of the mass and the positive charge of the atom are concentrated into a very small space at the centre of the atom, called the **nucleus** of the atom.

(iii) The electrons move around the positively charged nucleus in fixed circular paths, called **orbits** or energy levels.
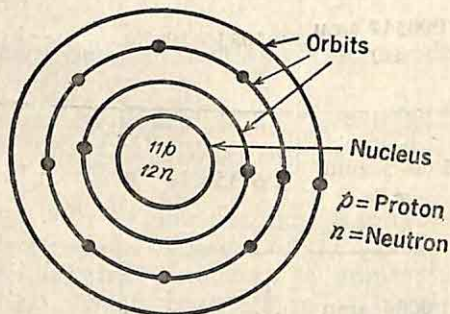
(iv) The volume occupied by the nucleus is negligible as compared to the volume of the atom.

Constitution of the Nucleus :

Atomic nuclei are made up of protons and neutrons bound together. The radius of the nucleus is very small, approximately

2×10^{-13} cm as compared to 10^{-8} cm for an atom (H-atom). As most mass of the atom is concentrated in the nucleus, its density is enormously high, approximately 10^{13} gm cm^3. The densities of different nuclei are almost the same.

Each nucleus contains a definite number of protons and the charge on the nucleus is determined by this number. For example, nucleus of H-atom contains one proton. Hence, the nuclear charge $= +1$. Similarly, the nucleus of Li atom contains 3 protons. Hence the nuclear charge $= +3$.

Atomic Number :

The number of nuclear charges in the atom of an element is known as the atomic number of the element.

Atomic number = Number of protons

= Number of nuclear charges.

The atomic number of an element is its most fundamental property. Atoms with the same atomic number may have somewhat different masses and still have almost identical other properties. But any change in atomic number causes a radical change in properties. Besides, the atomic number provides a basis for the modern Periodic classification of elements.

Mass Number :

The mass of the nucleus is determined by the number of protons as well as the number of neutrons. The total number of protons and neutrons is known as the mass number of a nucleus.

Mass number = Number of protons + Number of neutrons

or, $A = Z + n$.

Nucleons—The particles in the nucleus are collectively called nucleons and it is constituted of neutrons and protons.

Nature of forces in the nucleus :

Yukawa in 1935 postulated that π-mesons act as a cementing force binding the proton-proton, proton-neutron and neutron-neutron together. The π-meson may have a positive charge (π^+), a negative charge (π^-) or no charge (π^0). These π-mesons are continuously exchanged as follows :
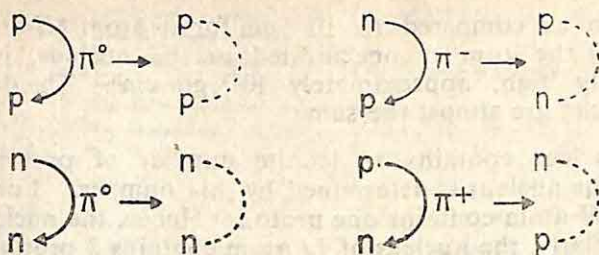
All mesons are very unstable outside the nucleus.

An atom is neutral, why ?

An electron has a charge equal but opposite in sign to that of a proton. As the number of protons in an atom is equal to the number of electrons, the total positive charge in the nucleus is equal to the total negative charge of all the electrons in the atom. Hence, an ordinary atom is electrically neutral.

Consider an oxygen atom. It has 8 protons in the nucleus and 8 extra nuclear electrons.

$\therefore$ Total positive charge $= +8$

Total negative charge $= -8$

$\therefore$ Net charge $= +8 + (-8) = 0$.

Defects in Rutherford's Model :

(i) According to Maxwell's theory, a charged particle moving

under the influence of an attractive force must emit electromagnetic radiation continuously. In giving out radiation an electron, which is a negatively charged particle, should continuously lose energy. Its orbit should, therefore, become steadily smaller, and in a very short time (nearly 10^{-10} second) it should collide with the nucleus. But we know that atomic electrons do not behave in this way.
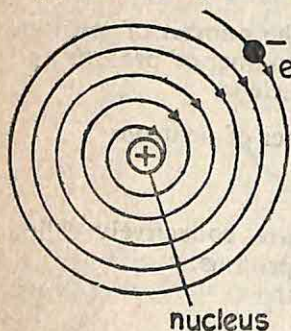
(ii) Rutherford's model does not explain the existence of line spectra.

Bohr's Theory :

To overcome the anomalous position of the Rutherford's model, Niel's Bohr proposed some postulates :

(i) An atom possesses several stable circular orbits in which an electron can revolve. So long as an electron stays in a particular orbit there is no emission or absorption of energy. These non-radiating orbits are called stationary orbits.

(ii) An electron can jump from lower energy level to a higher one on absorption of energy, or from higher energy level to a lower one on the emission of energy.

The absorption or emission of energy takes place in a fixed amount, the smallest being one quantum. Hence,

$$E_2 - E_1 = h\nu$$

where, ν is the frequency of emitted or absorbed light and $(E_2 - E_1)$ is the energy-difference between the two levels. In general, transitions of electrons from one orbit to another occur in integral multiples of $h\nu$. In other words, it is said that energy is quantised. Quantisation means that a quantity does not vary continuously.

n=4

n=3 $r_4 = 8 \cdot 5 A°$

n=2 $r_3 = 4 \cdot 8 A°$

n=1 $r_2 = 2 \cdot 1 A°$

$r_1 = 0 \cdot 53 A°$

nucleus

(iii) The angular momentum of an electron moving in an orbit is an integral multiple of $\frac{h}{2\pi}$. That is,

$$mvr = \frac{nh}{2\pi}$$

where, $n = 1, 2, 3, 4, \ldots$ for the orbits numbered $1, 2, 3, 4, \ldots$ from the nucleus and h is the Planck constant.

Radius and Energy of an Orbit :

Let us consider a circular orbit of radius r, and the linear velocity of an electron v, the mass of the electron being m. For an orbit to be stable, the centrifugal force produced by the moving electron must be equal to the attractive forces between the nucleus and the electron.

Centrifugal force $= \dfrac{mv^2}{r}$.
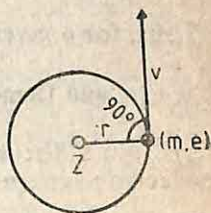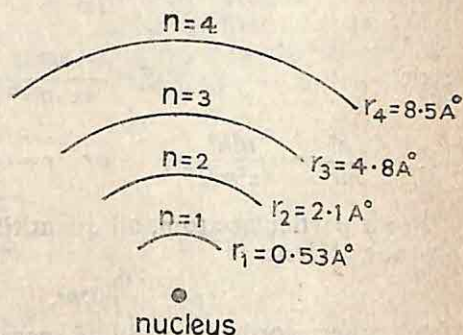
Electric force of attraction $= \dfrac{e^2}{r^2}$.

$$\therefore \quad \frac{mv^2}{r} = \frac{e^2}{r^2}, \quad \text{or} \quad v^2 = \frac{e^2}{mr} \qquad \qquad \text{.. (i).}$$

Now, according to the third postulate,

$$mvr = \frac{nh}{2\pi}$$

or

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \qquad \qquad \text{.. (ii).}$$

$$\therefore \quad \frac{e^2}{mr} = \frac{n^2h^2}{4\pi^2m^2r^2}, \quad \text{or} \quad r = \frac{n^2h^2}{4\pi^2e^2m}.$$

For a particular atom, all quantities on the R. H. S. except n is constant. Hence,

$$r \propto n^2.$$

In other words, the radii of successive orbits are proportional to the squares of the integers 1, 2, 3 ...., etc. These integers are called the **Principal Quantum Numbers**.

Total energy of the electron :

Total energy = K. E. + P. E.

$$= \frac{1}{2}mv^2 + V = \frac{e^2}{2r} - \frac{e^2}{r} = -\frac{e^2}{2r}.$$

Substituting the value of r,

$$E = -\frac{e^2}{2} \times \frac{4\pi^2me^2}{n^2h^2} = -\frac{2\pi^2me^4}{n^2h^2}$$

i. e.,

$$E \propto \frac{1}{n^2}.$$

Thus, for a given orbit the value of energy will remain constant.

Merits and Demerits of Bohr's Theory :

(i) Bohr's theory explains successfully the spectra of simple one-electron systems, such as H, He^+, Li^{++} etc.

(ii) Electronic transitions as predicted by Bohr's theory closely agree with those obtained experimentally by Rydberg.

(iii) The radius of the first orbit in hydrogen atom calculated from Bohr's theory is found to be in good agreement with the most

probable radius of the ground state predicted by Schrodinger wave model.

But the theory fails to explain the spectra of more complicated multi-electron atoms.

Bohr-Bury Scheme of the arrangement of electrons in various orbits of an atom :

The orbits in an atom are arranged circularly around the nucleus. The orbit nearest to the nucleus is called the first orbit ($n=1$) or K-shell, the next to this is called the second orbit or the L-shell for which $n=2$. Similarly, orbit numbers $n=3$, $n=4$, $n=5$ etc. are

designated as M, N, O, P, Q shells respectively. The number of electrons in these orbits is ascertained by Bohr-Bury scheme. According to this scheme :

(i) The maximum number of electrons in an orbit is determined by the formula $2n^2$, where n is the orbit number. Thus,

maximum-number of electrons in the 1st orbit $=2n^2=2\times1^2=2$

,,	,,	2nd	,,	$=2\times2^2=8$
,,	,,	3rd	,,	$=2\times3^2=18$
,,	,,	4th	,,	$=2\times4^2=32$

(ii) The maximum number of electrons to be accomodated in the outermost orbit cannot exceed 8, and the orbit preceding the outermost orbit (penultimate orbit) cannot contain more than 18 electrons.

(iii) The outermost orbit and the penultimate orbit cannot contain more than 2 and 9 electrons respectively unless the orbits preceding them are satisfied by rule (i).

In the light of this scheme the diagrammatic arrangement of electrons in orbits are given below :

Helium (He)

Neon (Ne)

Argon (Ar)

Fluorine (F)

Chlorine (Cl)

Oxygen (O)

Sulphur (S)

Nitrogen (N)

Phosphorus (P)

Carbon (C)

Silicon (Si)

Boron (B)

Aluminium (Al)

Beryllium (Be)

Magnesium (Mg)

Hydrogen (H)

Lithium (Li)

Sodium (Na)

Potassium (K)

Heisenberg's Uncertainty Principle :

According to this principle, the simultaneous determination of the position and momentum of an electron is impossible.

The product of uncertainties is equal to or greater that the Planck's constant 'h', i.e.,

$$\Delta x. \ \Delta y \geqslant \frac{h}{4\pi}.$$

where, Δx is the uncertainty in the determination of position, and Δy is the uncertainty in the dertermination of momentum.

This principle is now regarded as the fundamental principle of nature.

Wave Mechanical Concept of Atom :

Louis de Broglie (1923) introduced a new concept that electron possesses both corpuscular and wave character.

$$E = hv.$$

Also, $E = mc^2$, where $c =$ velocity of light.

$$\therefore \ hv = mc^2, \ \text{or} \ \frac{hc}{\lambda} = mc^2; \ (\because c = \lambda v)$$

or $\frac{h}{\lambda} = mc.$

For an electron let the velocity be v. Then,

$$\frac{h}{\lambda} = mv = p, \ \text{where} \ p \ \text{is momentum of the electron.}$$

$$\therefore \ \lambda = \frac{h}{p}.$$

This is de Broglie equation showing the particle as well as wave character of electron.

In wave mechanics the complete definition of an electron is given by a mathematical function called the wave function and the wave function of an electron is called an **orbital**.

Quantum Numbers :

Heisenberg, Schrödinger and Dirac (1925) developed a theory which governs the mechanics of a small particle like electron. This theory is called quantum mechanics or wave mechanics.

According to quantum mechanical theory of the atom a total of three quantum numbers, n, l and m is needed to specify the physical

state of the electron in a hydrogen atom. The role of the fourth quantum number, i.e. the spin quantum number(s) to specify the orientation of the axis of spin of the electron is also to be considered.

(1) **Principal quantum number** (*n*)—This gives an idea about the number of main energy levels in which the electron resides. It is denoted by *n*. The energy of transition of the electron from one circular orbit to another depends upon the value of *n*.

The value of *n* gives information about the energy of the electron and the size. Large *n* means large size. *n* can have any integral value 1, 2, 3, 4, etc. between 0 and ∞.

As *n* increases, the energy of the electron increases. The energy of an electron is expressed as

$$E = -\frac{2\pi^2 me^4 z^2}{n^2 h^2} \quad (n = \text{Principal quantum number}).$$

(2) **Azimuthal quantum number** (*l*)—Sommerfeld introduced a second quantum number called azimuthal quantum number to describe the ellipticity of orbits. It is denoted by *l* and it gives an idea regarding the shape of the orbital. It arises due to the orbital angular momentum given by :

$$mvr = \sqrt{l(l+1)} . \frac{h}{2\pi}$$

The azimuthal quantum number has the value from 0 to $(n-1)$. Thus, *l* can have *n* different values, where *n* is the number of the principal shell.

When $n = 1$, $l = 0$, i.e. one subshell.

When $n = 2$, $l = 0$, 1, i.e. two subshells.

When $n = 3$, $l = 0$, 1, 2, i.e. three subshells.

When $n = 4$, $l = 0$, 1, 2, 3, i.e. four subshells.

The subshells corresponding to $l = 0$, 1, 2 and 3 are called *s*, *p*, *d* and *f* subshells respectively.

The energy content of the subshells of a given shell increases in the order, $s < p < d < f$.

(3) **Magnetic quantum number** (*m*)—The subshells defined by definite *n* and *l* values in the presence of a magnetic field are further sub-divided. The sub-divisions are denoted by a third quantum number, known as **magnetic quantum number**, denoted by *m*.

This quantum number actually defines the orientations of the subshells in space.

m can have any integral value from $-l$ to $+l$ including 0. Thus, the total possible values of *m* will be $(2l+1)$.

If $l=0$, $m=0$.

,, $l=1$, $m=-1, 0, +1$.

,, $l=2$, $m=-2, -1, 0, +1, +2$.

,, $l=3$, $m=-3, -2, -1, 0, +1, +2, +3$.

All the possible orientations corresponding to $l=3$ are shown in figure given below :
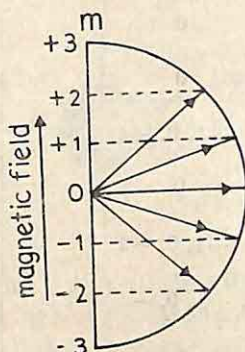
(4) **Spin quantum number** (s)—It has been assumed that each electron spins around its own axis like a top, thus behaves like a small magnet. A spinning electron can have only two possibilities. The electron can either spin clockwise or anti-clockwise.

(clockwise)   (anti-clockwise)
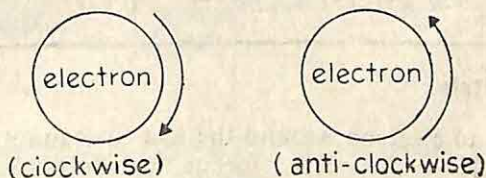
The two directions of spin are usually represented by arrows pointing upwards ($\uparrow$) or downwards ($\downarrow$). In order to account for the energy originated out of spinning of the electron, a fourth quantum number, known as **spin quantum number** (s) has been proposed.

Spin quantum number is independent of the other three quantum numbers, n, l and m. s can have two possible values $+\frac{1}{2}$ or $-\frac{1}{2}$ depending on the direction of spin. The spin angular momentum is given by :

$$\sqrt{s(s+1)}.\frac{h}{2\pi}.$$

Quantum numbers of Electrons

Principal quantum number (n)		Azimuthal quantum number (l)		Magnetic quantum number (m)	Spin quantum number (s)	Number of electrons, in each subshell	Total number of electrons
Number and Spectroscopic sign		Number and Symbol					
1	K	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	L	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
		1	p	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	8
3	M	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
		1	p	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	
		2	d	$+2, +1, 0, -1, -2$	$+\frac{1}{2}, -\frac{1}{2}$	10	18
4	N	0	s	0	$+\frac{1}{2}, -\frac{1}{2}$	2	
		1	p	$+1, 0, -1$	$+\frac{1}{2}, -\frac{1}{2}$	6	
		2	d	$+2, +1, 0, -1, -2$	$+\frac{1}{2}, -\frac{1}{2}$	10	
		3	f	$+3, +2, +1, 0, -1, -2, -3$	$+\frac{1}{2}, -\frac{1}{2}$	14	32

Atomic Orbitals :

The path of an electron around the nucleus cannot be described in terms of orbits. An orbit means a definite path which is not correct in the light of the uncertainty principle. The motion of electrons around the nucleus is described in terms of a set of mathematical expressions which allow for the dual behaviour of electrons. These expression are called orbital wave functions or simply orbitals denoted by the symbol Ψ.
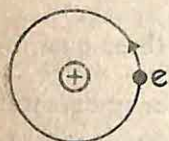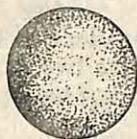
orbit

orbital

In the physical sense, an orbital is a region in space around the nucleus in which there is the maximum probability of the electron being located. This region is a cloud of negative charge.

However, it is difficult to depict the picture of an orbital.

Subshells and Orbitals :

The s-subshell (i.e., when $l=0$) has only one possible orientation (i.e., m has only one value) in space. This means that s-subshell has only one orbital and that is s-orbital. It is spherically symmetrical about the nucleus. The size of the s-orbital depends upon the value of the principal quantum number (n).
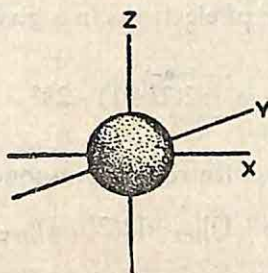
For p-subshell (i.e., when $l=1$), m has three values $(+1, 0, -1)$. Therefore, p-subshell has three possible orientations. This means that p-subshell has three orbitals. These orbitals are designated as p_x, p_y and p_z.
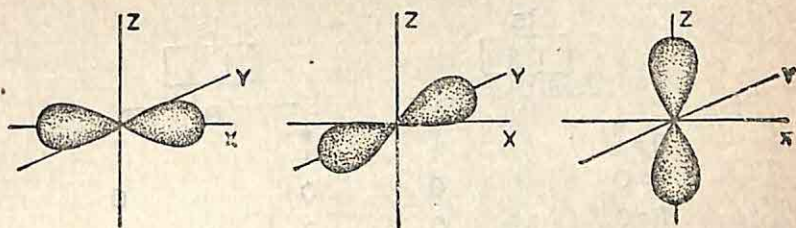
In the d-subshell (i.e., when $l=2$), m has five values $(+2, +1, 0, -1, -2)$. Therefore, d-subshell has five possible orientations. This means that d-subshell has five orbitals, being designated as d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}.

The f-subshell (i.e., when $l=3$) has seven values for m $(+3, +2, +1, 0, -1, -2, -3)$. Therefore, f-subshell has seven possible orientations. This means that f-subshell has seven orbitals. The designation and shape of these orbitals being complicated, would not be discussed at this stage.

Pauli's exclusion principle : This principle is stated as :

No two electrons in an atom can have all the four quantum numbers identical.

The principle has been found to be very useful in determining the maximum number of electrons in each shell.

Let the azimuthal quantum number be l.

$\therefore$ Possible values for magnetic quantum number $= (2l+1)$.

Now, l can have values ranging from 0 to $(n-1)$.

Hence, total number of electrons in a given shell

$$= \sum_{l=0}^{l=n-1} 2(2l+1) = 2n^2$$

Maximum number of electrons corresponding to $n=3$ is

$$= [2(2l+1)]_{l=0} + [2(2l+1)]_{l=1} + [2(2l+1)]_{l=2}$$
$$= 2 + 6 + 10 = 18$$

The configuration of $He(2)$ can be shown by any of the following two ways, A and B.
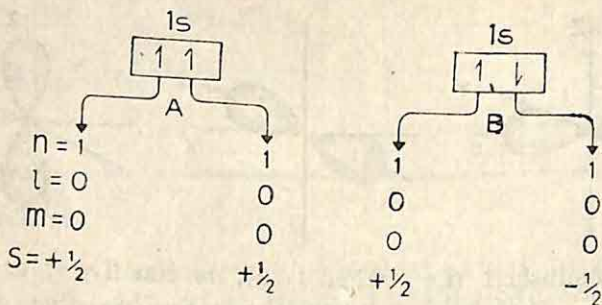
The configuration as shown in (A) is incorrect because both the electrons have the same set of quantum numbers which is contrary to Pauli's principle. In (B) the configuration is correct. In this case, the two electrons have n, l and m always the same but have different s values.

As a consequence of this principle, two is the maximum number of electrons permitted in an s-orbital, six in the three p-orbitals and 10 in the five d-orbitals. This can be shown as :

```
 n        l              m       s
 1────────0──────────────0<  +½  }1s=2
                             −½
 2───────0───────────────0<  +½  }2s=2
                             −½
                        +1<  +½
                             −½
          1<────────────0<   +½  }2p=3X2=6
                             −½
                        −1<  +½
                             −½
 3────────0──────────────0<  +½  }3s=2
                             −½
                        +1<  +½
                             −½
          1<────────────0<   +½  }3p=3X2=6
                             −½
                        −1<  +½
                             −½
                        +2<  +½
                             −½
                        −2<  +½
                             −½
          2<────────────0<   +½  }3d=5X2=10
                             −½
                        −1<  +½
                             −½
                        −2<  +½
                             −½
```
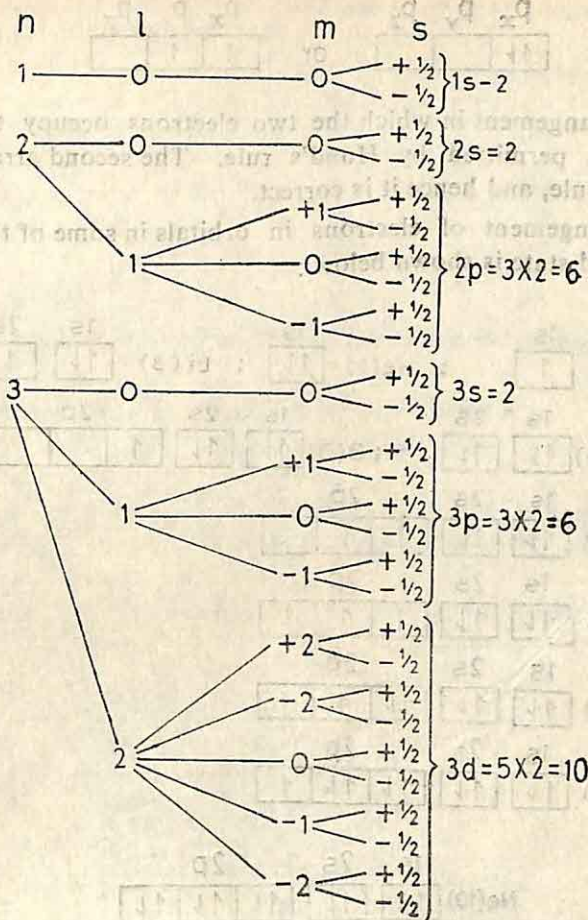
Hund's Rule : The electrons may be arranged into boxes. Each box represents an orbital. Thus s, p and d orbitals are shown as,

```
  s        p              d
┌──┐ ┌──┬──┬──┐ ┌──┬──┬──┬──┬──┐
│  │ │  │  │  │ │  │  │  │  │  │
└──┘ └──┴──┴──┘ └──┴──┴──┴──┴──┘
```

The three p orbitals are of identical energy. Similarly, the five d orbitals are of equivalent energy. Such orbitals are called 'degenerate orbitals'. According to Hund's rule, One electron is placed in all orbitals of equal energy (degenerate orbitals) before two electrons are placed in any one of the degenerate set and the electrons in the singly occupied orbitals have parallel spins.

If two electrons are to be added p-orbitals, there are two possible ways.

$$p_x \quad p_y \quad p_z \qquad\qquad p_x \quad p_y \quad p_z$$

| $1\downarrow$ | | | or | 1 | 1 | |
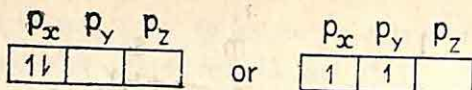
The first arrangement in which the two electrons occupy the same orbital is not permitted by Hund's rule. The second arrangement satisfies the rule, and hence it is correct.

The arrangement of electrons in orbitals in some of the atoms in the ground state is shown below :

H(1) 1s [1] ; He(2) 1s [1↓] ; Li(3) 1s [1↓] 2s [1]

Be(4) 1s [1↓] 2s [1↓] ; B(5) 1s [1↓] 2s [1↓] 2p [1 | |]

C(6) 1s [1↓] 2s [1↓] 2p [1 | 1 |]

N(7) 1s [1↓] 2s [1↓] 2p [1 | 1 | 1]

O(8) 1s [1↓] 2s [1↓] 2p [1↓ | 1 | 1]

F(9) 1s [1↓] 2s [1↓] 2p [1↓ | 1↓ | 1]

Ne(10) 1s [1↓] 2s [1↓] 2p [1↓ | 1↓ | 1↓]
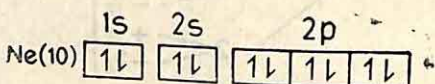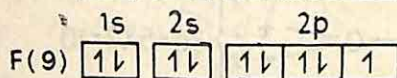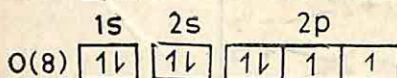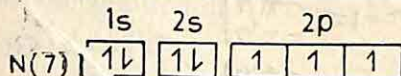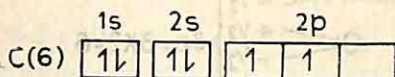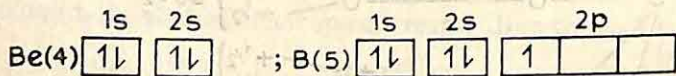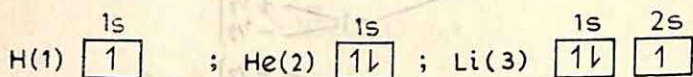
The combination of up and down spins ($\uparrow\downarrow$) is commonly called pairing of spins.

Aufbau Principle or Building-up Principle :

According to this principle, electrons are put into orbitals in order of the energy of the orbitals. The lowest energy orbitals are filled first before electrons are placed in higher energy orbitals.

The correct sequence of energy levels is derived on the basis of the following rules :

(i) The orbitals which have the lowest value of $(n+l)$ are the first to be occupied by electrons.

(ii) In case, the two orbitals have the same $(n+l)$ value. the one with the lower n is occupied first.

n	l	$(n+l)$	orbitals
1	0	1	$1s$
2	0	2	$2s$
2	1	3	$2p$
3	0	3	$3s$
3	1	4	$3p$
3	2	5	$3d$
4	0	4	$4s$
4	1	5	$4p$

$(n+l)$ value for $4s$ is smaller than $3d$, hence $4s$ is first filled up before $3d$.

The order of orbital energy is now established as,

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f.$$

This order is valid only for elements of lower atomic numbers. For elements with atomic numbers greater than 90, the following sequence holds :

$$1s < 2s < 2p < 3s < 3p < 3d < 4s < 4p < 4d < 4f < 5s < 5p < 5d < 5f < 6s < 6p < 6d < 7s < 7p.$$
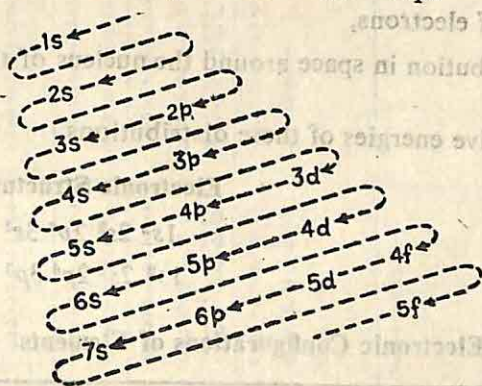
Screening Rule : This rule states that electrons filling the inner shells produce the screening effect on the outer electrons against attraction by the nucleus. For this reason, every ns orbital is filled earlier than the corresponding $(n-1)\,d$ orbital. Also, $5s$, $5p$ and $6s$ orbitals are filled earlier than $4f$ orbital.

Deviations from Aufbau Rule :

Some departure is obviously marked from the Aufbau rule. The departure comes in when d orbitals are either almost full

as in the case of *Cu, Pd, Ag, Pt and Au* or half-full as in *Cr* and *Mo*. These cases can be explained by the fact that **completely filled, completely half filled** and completely vacant arrangements are more stable than any other. Thus, d^5 and d^{10} configurations are more stable than d^4, d^8 and d^9. Consider the configuration $4d^4, 5s^2$ as shown below :

		4d				5s
1	1	1	1			1↓

If one electron moves from 5s to 4d the arrangement becomes :

		4d			5s
1	1	1	1	1	1

In this the 4d is completely half-filled. Hence this arrangement is preferred over all others.

Electronic Structure : The chemical behaviour of an atom is mainly controlled by its **electronic structure**. The term 'electronic structure' means :

(i) number of electrons,

(ii) the distribution in space around the nucleus of these electrons, and

(iii) the relative energies of these distributions.

Element	Electronic Structure
Na (11)	$1s^2\ 2s^2\ 2p^6\ 3s^1$
Cl (17)	$1s^2\ 2s^2\ 2p^6\ 3p^5$

Electronic Configurations of Elements

	At. No.	K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p 5d 5f	P 6s 6p 6d	Q 7s
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	2 1					
C	6	2	2 2					
N	7	2	2 3					
O	8	2	2 4					
F	9	2	2 5					

	At. No.	K	L		M			N				O				P			Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Ne	10	2	2	6															
Na	11	2	2	6	1														
Mg	12	2	2	6	2														
Al	13	2	2	6	2	1													
Si	14	2	2	6	2	2													
P	15	2	2	6	2	3													
S	16	2	2	6	2	4													
Cl	17	2	2	6	2	5													
A	18	2	2	6	2	6													
K	19	2	2	6	2	6		1											
Ca	20	2	2	6	2	6		2											
Sc	21	2	2	6	2	6	1	2											
Ti	22	2	2	6	2	6	2	2											
V	23	2	2	6	2	6	3	2											
Cr	24	2	2	6	2	6	5	1											
Mn	25	2	2	6	2	6	5	2											
Fe	26	2	2	6	2	6	6	2											
Co	27	2	2	6	2	6	7	2											
Ni	28	2	2	6	2	6	8	2											
Cu	29	2	2	6	2	6	10	1											
Zn	30	2	2	6	2	6	10	2											
Ga	31	2	2	6	2	6	10	2	1										
Ge	32	2	2	6	2	6	10	2	2										
As	33	2	2	6	2	6	10	2	3										
Se	34	2	2	6	2	6	10	2	4										
Br	35	2	2	6	2	6	10	2	5										
Kr	36	2	2	6	2	6	10	2	6										
Rb	37	2	2	6	2	6	10	2	6			1							
Sr	38	2	2	6	2	6	10	2	6			2							
Y	39	2	2	6	2	6	10	2	6	1		2							
Zr	40	2	2	6	2	6	10	2	6	2		2							
Nb	41	2	2	6	2	6	10	2	6	4		1							
Mo	42	2	2	6	2	6	10	2	6	5		1							
Tc	43	2	2	6	2	6	10	2	6	6		1							
Ru	44	2	2	6	2	6	10	2	6	7		1							
Rh	45	2	2	6	2	6	10	2	6	8		1							
Pd	46	2	2	6	2	6	10	2	6	10									
Ag	47	2	2	6	2	6	10	2	6	10		1							
Cd	48	2	2	6	2	6	10	2	6	10		2							
In	49	2	2	6	2	6	10	2	6	10		2	1						
Sn	50	2	2	6	2	6	10	2	6	10		2	2						
Sb	51	2	2	6	2	6	10	2	6	10		2	3						
Te	52	2	2	6	2	6	10	2	6	10		2	4						
I	53	2	2	6	2	6	10	2	6	10		2	5						

	At. No.	K	L	M	N	O	P	Q
		1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f	6s 6p 6d	7s
Xe	54	2	2 6	2 6 10	2 6 10	2 6		
Cs	55	2	2 6	2 6 10	2 6 10	2 6	1	
Ba	56	2	2 6	2 6 10	2 6 10	2 6	2	
La	57	2	2 6	2 6 10	2 6 10	2 6	2	
Ce	58	2	2 6	2 6 10	2 6 10	2 6 1	2	
Pr	59	2	2 6	2 6 10	2 6 10 1	2 6 1	2	
Nd	60	2	2 6	2 6 10	2 6 10 2	2 6 1	2	
Pm	61	2	2 6	2 6 10	2 6 10 3	2 6 1	2	
Sm	62	2	2 6	2 6 10	2 6 10 4	2 6 1	2	
Eu	63	2	2 6	2 6 10	2 6 10 5	2 6 1	2	
Gd	64	2	2 6	2 6 10	2 6 10 6	2 6 1	2	
Tb	65	2	2 6	2 6 10	2 6 10 7	2 6 1	2	
Dy	66	2	2 6	2 6 10	2 6 10 8	2 6 1	2	
Ho	67	2	2 6	2 6 10	2 6 10 9	2 6 1	2	
Er	68	2	2 6	2 6 10	2 6 10 10	2 6 1	2	
Tm	69	2	2 6	2 6 10	2 6 10 11	2 6 1	2	
Yb	70	2	2 6	2 6 10	2 6 10 12	2 6 1	2	
Lu	71	2	2 6	2 6 10	2 6 10 13	2 6 1	2	
Hf	72	2	2 6	2 6 10	2 6 10 14	2 6 2	2	
Ta	73	2	2 6	2 6 10	2 6 10 14	2 6 3	2	
W	74	2	2 6	2 6 10	2 6 10 14	2 6 4	2	
Re	75	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
Os	76	2	2 6	2 6 10	2 6 10 14	2 6 6	2	
Ir	77	2	2 6	2 6 10	2 6 10 14	2 6 7	2	
Pt	78	2	2 6	2 6 10	2 6 10 14	2 6 9	1	
Au	79	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
Hg	80	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
Tl	81	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
Pb	82	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2	
Bi	83	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3	
Po	84	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4	
At	85	2	2 6	2 6 10	2 6 10 14	2 6 10	2 5	
Rn	86	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
Fr	87	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
Ra	88	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
Ac	89	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2
Th	90	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2
Pa	91	2	2 6	2 6 10	2 6 10 14	2 6 10 1	2 6 1	2
U	92	2	2 6	2 6 10	2 6 10 14	2 6 10 2	2 6 1	2
Np	93	2	2 6	2 6 10	2 6 10 14	2 6 10 3	2 6 1	2
Pu	94	2	2 6	2 6 10	2 6 10 14	2 6 10 4	2 6 1	2
Am	95	2	2 6	2 6 10	2 6 10 14	2 6 10 5	2 6 1	2
Cm	96	2	2 6	2 6 10	2 6 10 14	2 6 10 6	2 6 1	2
Bk	97	2	2 6	2 6 10	2 6 10 14	2 6 10 7	2 6 1	2
Cf	98	2	2 6	2 6 10	2 6 10 14	2 6 10 8	2 6 1	2
En	99	2	2 6	2 6 10	2 6 10 14	2 6 10 9	2 6 1	2
Fm	100	2	2 6	2 6 10	2 6 10 14	2 6 10 10	2 6 1	2
Mv	101	2	2 6	2 6 10	2 6 10 14	2 6 10 11	2 6 1	2
Nm(?)	102	2	2 6	2 6 10	2 6 10 14	2 6 10 12	2 6 1	2
Lw	103	2	2 6	2 6 10	2 6 10 14	2 6 10 13	2 6 1	2
Ku	104	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 2	2
Ha	105	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 3	2

Ground State Electronic Configuration of Elements

An atom in its lowest energy state is said to be in the **normal** state or the **ground state**.

			1s
H	(1)	$1s^1$	↑
He	(2)	$1s^2$	↑↓

			1s	2s		2p	
Li	(3)	$1s^2\,2s^1$	↑↓	↑			
Be	(4)	$1s^2\,2s^2$	↑↓	↑↓			
B	(5)	$1s^2\,2s^2\,2p^1$	↑↓	↑↓	↑		
C	(6)	$1s^2\,2s^2\,2p^2$	↑↓	↑↓	↑	↑	
N	(7)	$1s^2\,2s^2\,2p^3$	↑↓	↑↓	↑	↑	↑
O	(8)	$1s^2\,2s^2\,2p^4$	↑↓	↑↓	↑↓	↑	↑
F	(9)	$1s^2\,2s^2\,2p^5$	↑↓	↑↓	↑↓	↑↓	↑
Ne	(10)	$1s^2\,2s^2\,2p^6$	↑↓	↑↓	↑↓	↑↓	↑↓

			3s	3p		
Na	(11)	$[Ne]\,3s^1$	↑			
Mg	(12)	$[Ne]\,3s^2$	↑↓			
Al	(13)	$[Ne]\,3s^2\,3p^1$	↑↓	↑		
Si	(14)	$[Ne]\,3s^2\,3p^2$	↑↓	↑	↑	
P	(15)	$[Ne]\,3s^2\,3p^3$	↑↓	↑	↑	↑
S	(16)	$[Ne]\,3s^2\,3p^4$	↑↓	↑↓	↑	↑
Cl	(17)	$[Ne]\,3s^2\,3p^5$	↑↓	↑↓	↑↓	↑
Ar	(18)	$[Ne]\,3s^2\,3p^6$	↑↓	↑↓	↑↓	↑↓

3d	4s	
□ □ □ □ □	↑	K (19) $[Ar]\,3d^0\,4s^1$
□ □ □ □ □	↑↓	Ca (20) $[Ar]\,3d^0\,4s^2$
↑ □ □ □ □	↑↓	Sc (21) $[Ar]\,3d^1\,4s^2$
↑ ↑ □ □ □	↑↓	Ti (22) $[Ar]\,3d^2\,4s^2$
↑ ↑ ↑ □ □	↑↓	V (23) $[Ar]\,3d^3\,4s^2$
↑ ↑ ↑ ↑ ↑	↑	Cr (24) $[Ar]\,3d^5\,4s^1$

3d	4s	
↑ ↑ ↑ ↑ ↑	↑↓	Mn (25) $[Ar]\,3d^5\,4s^2$
↑↓ ↑ ↑ ↑ ↑	↑↓	Fe (26) $[Ar]\,3d^6\,4s^2$
↑↓ ↑↓ ↑ ↑ ↑	↑↓	Co (27) $[Ar]\,3d^7\,4s^2$
↑↓ ↑↓ ↑↓ ↑ ↑	↑↓	Ni (28) $[Ar]\,3d^8\,4s^2$
↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	Cu (29) $[Ar]\,3d^{10}\,4s^1$
↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	Zn (30) $[Ar]\,3d^{10}\,4s^2$

Valence Electrons : The number of electrons in the outermost shell of an atom determines the maximum valency of the element. These electrons are called **valence electrons.**

Core Electrons : The electrons occupying the inner shells preceding the outermost one are called **core electrons.**

For example, in the Na atom there is only one valence electron, but there are 10 core electrons.

Na (11) $1s^2 2s^2 2p^6 3s^1$
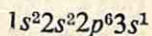
V. E. $= 1$

Core electrons $= 10$

The valence electrons take part in all chemical reactions and they determine the chemical reactivity of the element.

Kernel : The nucleus plus the low-energy electrons, except the electrons in the outermost shell, that are never affected by a chemical change, is called the 'Kernel' of the atom.

Magnetic Properties of Atoms :

Atoms exhibit magnetic properties. There are two kinds of magnetism :

(i) Diamagnetism and (ii) Paramagnetism.

Diamagnetism—Atoms, ions or molecules containing only paired electrons or completely filled orbitals exhibit diamagnetism. For example, Ca atom and Ca^{++} ion both are diamagnetic because all their electrons are paired.
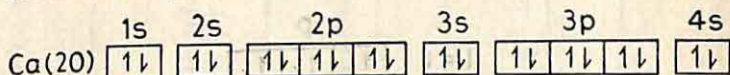
With paired electrons the spin and orbital magnetic effects are completely cancelled. Hence, electron pair becomes unresponsive to an external magnetic field.

Paramagnetic—Atoms, ions or molecules containing unpaired electrons exhibit paramagnetism. For example, Na atom is paramagnetic.
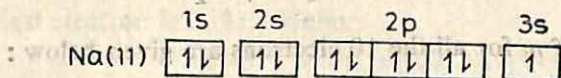
With unpaired electrons the spin and the orbital magnetic effects are not completely cancelled. Hence, in an externally applied magnetic field, the magnetic moments of such atoms are aligned in a particular direction.

The greater the number of unpaired electrons in an atom, the greater is the paramagnetism.

Atoms with odd atomic number have atleast one unpaired electron.

Determination of Quantum Numbers for an Electron :

In order to completely identify an electron all the four quantum numbers (n, l, m, s) are needed. The following guidelines should be adopted to know the values of n, l, m and s for an electron :

(i) Write down the electronic configuration of the atom, and get the values of n and l directly. As an example,

$$O(8) \qquad 1s^2 2s^2 2p^4$$
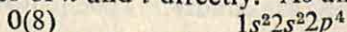
Suppose we have to know the values of n and l for the last electron. Evidently, the last electron lives in the p-subshell. Thus, for this electron, $n=2$ and $l=1$.

(ii) The values of the magnetic quantum number is determined from the value of l for the electron.

When $l = 0$ (i.e., p-subshell), $m = 0$

This means that both the electrons in the s-subshell have
$$m = 0.$$

When $l = 1$ (i.e., p-subshell), $m = +1, 0 - 1.$

$$l = 1 \quad \boxed{1\downarrow} \; \boxed{1\downarrow} \; \boxed{1\downarrow}$$
$$m = \quad +1 \quad\;\; 0 \quad\; -1$$
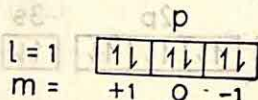
Thus, for the first and the fourth electron the value of $m = +1$, for the second and the fifth electron $m = 0$, and for the third and the sixth electron $m = -1$.

When $l = 2$ (i.e., d-subshell), $m = +2 +1, 0 -1.$

$$l = 2 \quad \boxed{1\downarrow}\;\boxed{1\downarrow}\;\boxed{1\downarrow}\;\boxed{1\downarrow}\;\boxed{1\downarrow}$$
$$m = \quad +2 \;\; +1 \;\; 0 \;\; -1 \;\; -2$$
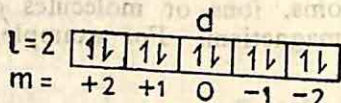
The values of m for all the 10 electrons are given below :

Electron number	m
1, 6	+2
2, 7	+1
3, 8	0
4, 9	−1
5, 10	−2

The evaluation of m for electrons in the f-subshell can be done similarly.

(iii) We know that an orbital can accomodate a maximum of two electrons having opposed spin. Hence, the values of the spin quantum number(s) for the electron spinning clockwise and that spinning anti-clockwise are given as $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively.

Examples : 1. Find the values of quantum numbers for all the electron in $Ne(10)$.

Solution :

$$\begin{array}{ccccc} 1s & 2s & & 2p & \\ \boxed{1\downarrow} & \boxed{1\downarrow} & \boxed{1\downarrow} & \boxed{1\downarrow} & \boxed{1\downarrow} \end{array}$$
$$\begin{array}{ccccc} 1\;\;2 & 3\;\;4 & 5\;\;8 & 6\;\;9 & 7\;10 \end{array}$$
$$m = \;\; 0 \quad\quad 0 \quad\quad +1 \quad\;\; 0 \quad\;\; -1$$
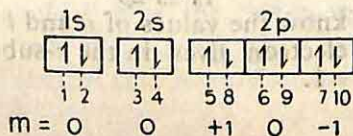
Electron Number	Quantum Number			
	n	l	m	s
1	1	0	0	$+\frac{1}{2}$
2	1	0	0	$-\frac{1}{2}$
3	2	0	0	$+\frac{1}{2}$
4	2	0	0	$-\frac{1}{2}$
5	2	1	$+1$	$+\frac{1}{2}$
6	2	1	0	$+\frac{1}{2}$
7	2	1	-1	$+\frac{1}{2}$
8	2	1	$+1$	$-\frac{1}{2}$
9	2	1	0	$-\frac{1}{2}$
10	2	1	-1	$-\frac{1}{2}$

2. Find the values of all the quantum numbers for the valence electron in $Na(11)$.
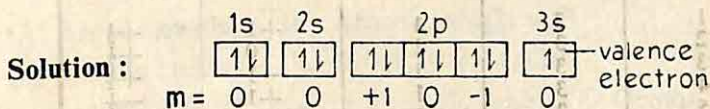
Solution :

The last electron is in $3s$. Hence,

$$n=3; \quad l=0; \quad m=0; \quad s=+\tfrac{1}{2}$$

Some Illustrative Problems :

1. An atom of an element contains 13 electrons and 14 neutrons. Find the mass number and atomic number of the element.

Solution : Mass number = Number of protons + Number of neutrons.

= Number of electrons + Number of neutrons = $13+14=27$.

Atomic Number = Number of protons.

= Number of electrons = 13.

2. The atomic number of an element is 16 and its atomic mass is 32. What will be the atomic structure of the element ?

Solution : Atomic number = Number of protons

= Number of electrons = 16.

Number of neutrons = Atomic mass − Atomic number

= $32-16=16$.

3. Write down the electronic configuration of the following elements :

(a) Cr (24),   (b) Cu (29),   (c) Ag (47).

Ans. (a) Cr (24) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

(b) Cu (29) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

(c) Ag (47) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^1$

4. Write all the four quantum number for all the $3p^6$ electrons.

All the six electrons are as labelled above. For all the electrons $n = 3$ and $l = 1$

Electron Number	n	l	m	s
1	3	1	$+1$	$+\frac{1}{2}$
2	3	1	0	$+\frac{1}{2}$
3	3	1	-1	$+\frac{1}{2}$
4	3	1	$+1$	$-\frac{1}{2}$
5	3	1	0	$-\frac{1}{2}$
6	3	1	-1	$-\frac{1}{2}$

5. Determine all the four quantum numbers for the last electron entering the Cl atom.

Ans. The pictorial representation of Cl (17) atom is as follows :

The last electron is in $3p$ and indicated by a downward. dotted arrow line at the end.

Thus, $n = 3$, $l = 1$, $m = -1$ and $s = -\frac{1}{2}$.

6. Write the names of orbitals for which (a) $n = 2$, l 0; (b) $n = 2$, $l = 1$; (c) $n = 4$, $l = 3$; (d) $n = 4$, $l = 4$, $l = 2$ and (e) $n = 4$, $l = 1$.

Ans. (a) $2s$, (b) $2p$, (c) $4f$, (d) $4d$ and (e) $4p$.

7. The nucleus of an atom of an element contains 20 neutrons and 20 protons. What will be the atomic weight, atomic number and valency of the element ?   **(I.I.T. Entrance Exam.)**

Solution : Mass number (or atomic weight)

= Number of protons + Number of neutrons = $20 + 20 = 40$.

Atomic number = Number of protons = 20.

Electronic configuration : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

∴ Valency = 2

8. An element A has atomic number 10 and atomic weight 20, while another element B has atomic number 19 and atomic weight 39. Give :

(a) Their position in the periodic table.

(b) The arrangement of electrons in the extra-nuclear structures of their atoms.

(c) The number of neutrons in the nuclei of their atoms.

(d) What type of valency these elements exhibit ?

(**I.I.T. Entrance Exam.**)

Solution :

(A) Atomic number = 10. Atomic weight = 20

(B) Atomic number = 19, Atomic weight = 39

(a) Position of A in the periodic table is O Group.
Position of B in the periodic table is I Group.

(b) Arrangement of electrons in A : 2, 8
Arrangement of electrons in B : 2, 8, 8, 1.

(c) No. of Neutrons in A = 10
No. of Neutrons in B = 39 − 19 = 20.

(d) A will exhibit zero valency, while B electro-valency.

9. A rifle bullet of $2 \cdot 2 \times 10^{-3}$ kg is shot with a velocity of 3×10^2 m sec^{-1}. Calculate its de Broglie wavelength.

Solution :
$$\lambda = \frac{h}{p} = \frac{\text{Planck constant}}{\text{momentum}}$$

$$= \frac{6 \cdot 6 \times 10^{-34}}{2 \cdot 2 \times 10^{-3} \times 3 \times 10^2}$$

$$= 1 \times 10^{-33} m.$$

10. Calculate the uncertainty in velocity ($\triangle y$) of an electron, if the uncertainty in its position ($\triangle x$) is $2 \times 10^{-10} m$ (2 angstrom unit).

Solution :

$$\therefore\ \triangle x.\ \triangle y = \frac{h}{4\pi}$$

Or, $\triangle y = \dfrac{h}{4\pi} \times \dfrac{1}{\triangle x}$

Or, $m \times \triangle v = \dfrac{6 \cdot 6 \times 10^{-34}}{4 \times 3 \cdot 1416} \times \dfrac{1}{2 \times 10^{-10}}$

Or, $\triangle v = \dfrac{6 \cdot 6 \times 10^{-34}}{m \times 4 \times 3 \cdot 1416} \times \dfrac{1}{2 \times 10^{-10}}$

$= \dfrac{6 \cdot 6 \times 10^{-34}}{9 \cdot 1 \times 10^{-31} \times 4 \times 3 \cdot 1416} \times \dfrac{1}{2 \times 10^{-10}}$

$= 2 \cdot 885 \times 105 m \text{ sec}^{-1}.$

Questions

Long Answer Type :

1. Describe the modern concept of the structure of atom.   (B.U. 1972A)

2. What is Rutherford's atomic model ? What are the defects in Rutherford's nuclear theory ?

3. Describe Bohr-Bury scheme for the arrangement of electrons in shell.
                                                                (M.U. 1974A)

4. Explain what you understand by the term atomic number. "Atomic number is the fundamental property of an atom", justify this statement.

5. Name the fundamental particles constituting the atom and give their relative and absolute masses and charges.

6. Write notes on **electron, proton** and **neutron.** How are the numbers of these particles related to atomic number and atomic mass ?

7. Discuss briefly the wave and particle nature of light.

8. What was the objection to Rutherford's model of the atom ? Discuss the solution proposed by Bohr to overcome this objection.

9. What do you mean by quantisation of energy ? Explain how Bohr used the quantum theory to postulate a stable atom.

10. Name the four quantum number which are needed to define completely the state of an electron. What is meant by Pauli's exclusion principle ?

11. State Pauli's exclusion principle. Explain how this principle has been used to determine the maximum number of electrons in a quantum shell.

12. State and explain the rules which govern the filling of electrons in various subshells in an atom. On the basis of these rules write the electronic configurations of the following elements :

    Sc (21), F (9), Al (13), S (61), Ar (18).

13. Write short notes on :

    (i) Hund's rule, (ii) Heisenberg's uncertainty principle, (iii) Aufbau principle.

14. A neutral atom has a ground state electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^2$. Deduce as many of the following as you can from this information only :

   (a) the atomic number of the element,

   (b) the atomic weight of the element,

   (c) the number of electrons in the valence shell,

   (d) the number of unpaired electrons in the atom.

15. Draw the electronic structures of the atoms of the elements having the following atomic numbers :

$$7, 10, 29, 33 \text{ and } 42.$$

16. Find the numerical values of the n, l, m and s for the last electron in the ground state of the following atoms :

$$Ne~(10),~Si~(14),~Cl~(17) \text{ and } Mn~(25).$$

17. How does the size of an atom vary when it changes to anion or to cation ?

Short Answer Type :

1. What is difference between an orbit and an orbital ?

2. Explain what is meant by a shell and a subshell.

3. Why is the Bohr theory incompatible with the uncertainty principle ?

4. In the Bohr model of the atom, what forces are involved in holding an electron in its orbit ?

5. How would you distinguish the Bohr model and the wave mechanical model of the atom ?

6. Define atomic number.

7. Define the term atomic mass in terms of the fundamental particles of the atom.

8. What is difference between s-orbital and p-orbital ?

9. Show that the maximum number of electrons in the M-shell is 18.

10. Give the shapes of p-orbitals.

11. Determine the number of protons, neutrons and electrons in the atoms of C^{12} and C^{14}. Give the electronic configurations also   **(I.I.T. 1977)**

12. What is Hund's rule ? Explain.   **(B.U. 1979A)**

13. What informations are obtained from the magnetic quantum number ?   **(B.U. 1979A)**

14. Explain Pauli's principle with reference to He configuration.   **(B.U. 1978A)**

15. What are valence electrons ?

16. Give reasons for the fact that the energy of the $1s$ electron is less than that of the $2s$ electron of the same atom.   **(B.U. 1978A)**

17. Write the electronic configurations of A^{++}; B^- and C. (Atomic numbers of A, B and C are 12, 17 and 18 respectively.)   **(B.U. 1979A)**

18. The atomic number of an atom is 8 and its atomic weight is 16. Find out (a) the number of neutrons in the nucleus of the atom, (b) its probable oxidation number, (c) its outer electronic configuration and (d) Whether it is a metal or a non-metal.   **(Bombay F. Yr. 1974)**

19. An atom has the electronic configuration $1s^2\ 2s^2\ 2p^2x\ 2p^2y\ 2p^2z\ 3s^2\ 3p^2x$ $3p^2y\ 3p^2z\ 4s^1$. What is its atomic number ? **(Pb : Pre. Engg./Pre. Med. 1974)**

20. To which element do each of the following electronic configuration corresponds :

(a) $1s^2 2s^1$,   (b) $1s^2 2s^2 2p^1$,   (c) $1s^2 2s^2 2p^1$,   (d) $1s^2 2s^2 2p^2$,   (e) $1s^2 2s^2 2p^4$,
(f) $1s^2 2s^2 2p^6$.   **(I.I.T. Entrance Exam.)**

21. Identify the atoms having the following configurations :

                        1s   **2s**   **2p**

(i)   [↑↓] [↑↓] [↑][   ][   ]

(ii)   [↑↓] [↑↓] [↑↓][↑][↑]

(iii)   [↑↓] [↑↓] [↑][↑][↑]
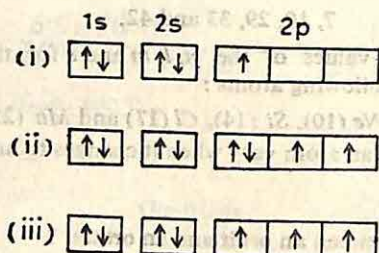
22. Name the scientists who gave the relationships :

    (i) $\triangle x \cdot \triangle y \geqslant \dfrac{h}{4\pi}$,   (ii) $E = h\nu$,   (iii) $\nu\lambda = \dfrac{h}{mv}$.

23. Explain why :

   (i) Cr has the outer electronic configuration $4s^1\ 3d^5$ and not $4s^2\ 3d^4$.

   (ii) Cu has the outer electronic configuration $4s^1\ 3d^{10}$ and not $4s^2\ 3d^9$.

   (iii) K has the electronic configuration $1^2s\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ and not $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1$.

24. Explain why half filled and completely filled orbitals have extra stability.

Objective Questions :

   (A) To each question below four answers are given, of which only one is correct. Choose the correct answer :

1. In the compound of an element whose atomic number is 11, the valency of the element is

    (i) -1,   (ii) $+2$,   (iii) $+1$,   (iv) -2.

2. To which of the following electronic configurations does an atom of Ca correspond to

    (i) $1s^2\ 2s^2\ 2p^6\ 3s^2$, (ii) $1s^2\ 2s^2$, (iii) $1s^2\ 2s^2\ 2p^6$, (iv) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$.

3. The atomic weight of an element is 23 and its atomic number is 11. The number of neutrons in the nucleus of an atom of the element is

    (i) 23,   (ii) 11,   (iii) 12,   (iv) 34.

4. The atomic number of an element is equal to

    (i) the number of an extranuclear electrons.

    (ii) the number of protons in the nucleus.

(iii) the number of neutrons in the nucleus.

(iv) the number of valence electrons.   **(Engg. Adm. Test)**

5. If the main quantum shell is denoted by n then the maximum number of electrons to be accomodated in this shell will be

(i) n^2,   (ii) $2n^2$,   (iii) n^3,   (iv) n.   **(Engg. Adm. Test)**

6. The electrons first fill up in

(i) s-orbital,   (ii) p-orbital,   (iii) f-orbital,   (iv) d-orbital.   **(R.U. 1977A)**

7. Which are the fundamental particles of an atom ?

(i) Electron, Positron and Neutron.

(ii) Electron, Proton and Neutron.

(iii) Proton, Meson and Antiproton.

(iv) Antineutron, Antiproton and Electron.

8. Which of the following is the heaviest particle ?

(i) electron,   (ii) proton;   (iii) neutron,   (iv) meson.

9. Which of the following has got no neutron ?

(i) C,   (ii) O,   (iii) N,   (iv) H.

10. The number of protons in the nucleus of an atom is called its

(i) mass number   (ii) atomic number   (iii) atomic weight

(iv) equivalent weight.

11. The sum of the numbers of protons and neutrons in the nucleus of an atom is called its

(i) avogadro's number (ii) mass number (iii) molecular mass (iv) avogram.

12. The total number of neutrons present in the divalent calcium ion $(Z=20)$ having mass number 42 is

(i) 20   (ii) 21   (iii) 22   (iv) 18.

13. An atom with atomic number 18 and mass number 40 will have the following number of protons (p), electrons (e) and neutrons (n) :

(i) $18p$, $18e$, $22n$

(ii) $18p$, $18e$, $40n$

(iii) $22p$, $18e$, $18n$

(iv) $22p$, $22e$, $18n$.

14. The fundamental particle responsible for keeping the nucleous together is

(i) meson   (ii) antiproton   (iii) positron   (iv) antineutron.

15. The maximum number of electrons in M shell is

(i) 2   (ii) 8   (iii) 32   (iv) 18.

16. The maximum number of electrons in any orbit is determined by

(i) $2n$ (ii) n^2 (iii) $2n^2$ (iv) $2^2 xn$.

17. Which of the following represents the arrangements of electrons for an element with atomic number 26 ?

(i) 2, 8, 16;   (ii) 2, 8, 8, 8;   (iii) 2, 8, 15, 1;   (iv) 2, 8, 24, 2.

INTR. CHEM.-3

18. The shape of s-orbital is

   (i) Dumb-bell, (ii) Spherical, (iii) Cylindrical, (iv) None of the above.

19. An 1s-orbital is described by the following values of quantum numbers :

   (i) $n=0, l=0$; (ii) $n=0, l=1$; (iii) $n=1, l=1$; (iv) $n=1, l=0$.

20. Which of the following represents the values of n, l and m for the last electron in chlorine atom ?

   (i) $n=3, l=1, m=0$; (ii) $n=3, l=2, m=0$; (iii) $n=3, l=1, m=+1$; (iv) $n=3, l=1, m=-1$.

21. Name the element having electronic configuration. $1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^2$

   (i) Carbon, (ii) Magnesium, (iii) Aluminium, (iii) Silicon.

22. In an atom of an element $2K$, $8L$ and $2N$ electrons are present. The total number of s-electrons will be

   (i) 2, (ii) 4, (iii) 6, (iv) 8.

23. An element has the electronic configuration $1s^2 \, 2s^2 \, 2p^6 \, 3s^3 \, 3p^2$. The number of valence electrons will be

   (i) 2, (ii) 3, (iii) 4, (iv) 6.

24. The principal quantum number indicates

   (i) the size of the orbit, (ii) ellipticity of the orbit, (iii) orientation of the orbit, (iv) none of these.

25. It is impossible to know simultaneously the position and the velocity of an electron. This statement is known as

   (i) Pauli's exclusion principle.

   (ii) Heisenberg's uncertainty principle.

   (iii) Hund's rule.

   (iv) Aufbau principle.

26. An oxygen atom contains

   (i) 4 neutrons and 8 protons.

   (ii) 8 protons and 2 neutrons.

   (iii) 8 protons and 16 electrons.

   (iv) 8 protons and 8 electrons.

   (v) 16 protons and 8 electrons. (P. M. D. T. 1976)

27. Chloride ion has the following number of electrons in its outermost orbit :

   (i) 1, (ii) 2, (iii) 4, (iv) 7, (v) 8.

28. An atom has the electronic configuration $1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, ?d^{10} \, 4s^2 \, 4p^6$. The most probable valence number for the atom is

   (i) -1, (ii) $+1$, (iii) $+2$, (iv) -2.

29. Bohr model of an atom is based on

   (i) quantum theory, (ii) Dalton's atomic theory, (iii) theory of electrolytic dissociation, (iv) law of mass action.

30. Two elements A and B having atomic masses 40 and 42 respectively are isotonic. If atomic number of B is 20, then the atomic number of A is

    (i) 21,   (ii) 20,   (iii) 19,   (iv) 22,   (v) 25.

31. Consider these two electron populations for neutral atoms

    $A.\ 1s^2\ 2s^2\ 2p^6\ 3s^1$, $B.\ 1s^2\ 2s^2\ 2p^6\ 6s^1$.

    Which of the following is FALSE ?

    (i)   Energy is required to change A to B.

    (ii) A and B represent different elements.

    (iii) B represents an atom in the excited state.

    (iv) Less energy is required to remove one electron from B than from A.

                        (A.I.I.M.S. and Medical Entrance 1981)

32. The spectrum of Li^+ may be expected to be similar to

    (i) H,   (ii) Be,   (iii) Na^+,   (iv) He.

33. According to classical theory, if an electron is initially moving is a circulae orbit around a nucleus :

    (i)   it will continue to do so for some time.

    (ii) it will continue to do so all time.

    (iii) its orbit will continuously shrink.

    (iv) its orbit will continuously enlarge.

(B) **Mark 'T' for the true statement and 'F' for the false statement in the following :**

1. The nucleus of an atom consists of protons and neutrons.   ( )
2. The maximum number of electrons in the d subshell is 8.   ( )
3. The energy of the $3d$ subshell is less than that of the $4s$ subshell.   ( )
4. The p-subshell has only one orientation in space.   ( )
5. The number of subshells in an orbit is equal to the orbit number.   ( )
6. The simultaneous determination of position and velocity accurately of an electron is impossible.   ( )
7. Pairing of electrons can be done only when all the available empty orbitals have attained at least one electron each.   ( )

    Answers :

    (A)   1. (iii)   2. (iv)   3. (iii)   4. (ii)   5. (ii)   6. (i)
           7. (ii)   8. (ii)   9. (iv)   10. (ii)   11. (ii)   12. (iii)
           13. (i)   14. (i)   15. (iv)   16. (iii)   17. (iv)   18. (ii)
           19. (iv)   20. (i)   21. (iv)   22. (iii)   23. (iii)   24. (i)
           25. (ii)   26. (iv)   27. (v)   28. (i)   29. (i)   30. (i)
           31. (ii)   32. (iv)   33. (iii).

    (B)   1. T   2. F   3. F   4. F   5. T   6. T   7. T.

□ □ □

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20. Which of the following represents the values of n, l and m for the last electron in chlorine atom ?

   (i) $n=3, l=1, m=0$;   (ii) $n=3, l=2, m=0$;   (iii) $n=3, l=1, m=+1$; (iv) $n=3, l=1, m=-1$.

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31. Consider these two electron populations for neutral atoms

A. $1s^2 2s^2 2p^6 3s^1$,   B. $1s^2 2s^2 2p^6 6s^1$.

Which of the following is FALSE ?

(i) Energy is required to change A to B.

(ii) A and B represent different elements.

(iii) B represents an atom in the excited state.

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(iii) its orbit will continuously shrink.

(iv) its orbit will continuously enlarge.

(B) Mark 'T' for the true statement and 'F' for the false statement in the following :

1. The nucleus of an atom consists of protons and neutrons.   ( )
2. The maximum number of electrons in the d subshell is 8.   ( )
3. The energy of the $3d$ subshell is less than that of the $4s$ subshell.   ( )
4. The p-subshell has only one orientation in space.   ( )
5. The number of subshells in an orbit is equal to the orbit number.   ( )
6. The simultaneous determination of position and velocity accurately of an electron is impossible.   ( )
7. Pairing of electrons can be done only when all the available empty orbitals have attained at least one electron each.   ( )

Answers :

(A)   1. (iii)   2. (iv)   3. (iii)   4. (ii)   5. (ii)   6. (i)
       7. (ii)   8. (ii)   9. (iv)   10. (ii)   11. (ii)   12. (iii)
       13. (i)   14. (i)   15. (iv)   16. (iii)   17. (iv)   18. (ii)
       19. (iv)   20. (i)   21. (iv)   22. (iii)   23. (iii)   24. (i)
       25. (ii)   26. (iv)   27. (v)   28. (i)   29. (i)   30. (i)
       31. (ii)   32. (iv)   33. (iii).

(B)   1. T   2. F   3. F   4. F   5. T   6. T   7. T.

■ □ □

CHAPTER 2

THE CHEMICAL BONDING

The force with which two elements are held together is known as a **chemical bond**. The atomic properties which operate in the formation of a bond are the following :

(A) Ionization Potential—The energy required to remove the most loosely bound electron from an isolated gaseous atom is called the **ionization potential**.

$$M \to M^+ + e, \text{ 1st. I.P.}$$
$$M^+ \to M^{2+} + e, \text{ 2nd. I.P.}$$
$$M^{2+} \to M^{3+} + e, \text{ 3rd. I.P.}$$
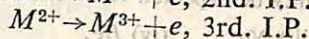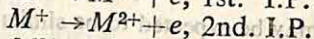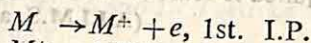
If the I.P. of an atom is small, the electron can be easily removed. If the I.P. is large, the removal of electron from the atom is difficult. The 2nd I.P. is always greater than the 1st I.P. This means, that the energy required to remove an electron from $M^+(g)$ is higher than that required to remove the electron from $M(g)$.

The factors on which the ionization potential depends are :

(i) size of the atom,
(ii) charge on the nucleus,
(iii) screening effect of inner electron shells and
(iv) type of electron involved.

These factors are inter-dependent.

In a small atom, the electrons are tightly held, but the larger the atom, the less tightly are the electrons held. Thus, the I.P. decreases with increase in size. In group I of the periodic table I.P. decreases as we go down from top to bottom.

The inner shells of electrons help to screen the outer electron from the attraction of the nucleus.

Greater the effective nuclear charge, higher is the value of the I.P. The 2nd I.P. of Na is greater than the 1st one. This is because in Na^+ ion the effective nuclear charge is increased. Similarly, the 1st I.P. of $Mg >$ the 1st I.P. of Na. This is partly due to the increased nuclear charge and partly due to the smaller size of magnesium.

I.P. also depends on the type of electron involved. The s electron penetrates nearer to the nucleus than p, d or f electrons, and hence it is more strongly held. The I.P. decreases in the order,

$$s > p > d > f.$$
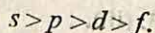
(B) Electron Affinity—The energy released when an electron is added to a neutral gaseous atom is called the **electron affinity**.

$$X(g) + e \to X^-(g) + E_A.$$
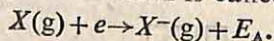
One electron is usually added forming a uni-negative ion (X^-). This repels further electrons and some energy is needed to add on a second electron. Hence, the electron affinity of O^{--} is negative.

Electron affinity depends on size and effective nuclear charge. If the size of the atom is large the added electron will be away from the nucleus and the nuclear attraction will be weak and hence the energy released will be quite small. That is why, the electron affinity of Br is lower than that of Cl.

High value of electron affinity means the element takes up electron easily to form an anion.

Chemical Inertness of the Noble Gases—The noble gases are : $He(2)$, $Ne(10)$, $Ar(18)$, $Kr(36)$, $Xe(54)$ and $Rn(86)$. The electronic configurations of these gases are given below :

He $(Z=2)$	$1s^2$
Ne $(Z=10)$	$1s^2\ 2s^2 2p^6$
Ar $(Z=18)$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6$
Kr $(Z=36)$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^{10}\ 4s^2 4p^6$
Xe $(Z=54)$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^{10}\ 4s^2 4p^6 4d^{10}\ 5s^2 5p^6$
Rn $(Z=86)$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6\ 3d^{10}\ 4s^2 4p^6 4d^{10} 4f^{14}\ 5s^2 5p^6 5d^{10}\ 6s^2 6p^6$

It is seen that the outermost electronic configuration of the noble gases is $ns^2 np^6$ (for He it is $1s^2$).

The ionisation potential of the noble gases is very high. So these elements have a little tendency to form cations by the loss of electrons. Similarly, the electron affinity of these elements being very small (almost zero) they cannot form anions by the gain of electrons. It is thus concluded that the **electronic configuration of the noble gases is very stable**. As there are eight electrons in the outermost orbit, it is reasonable to assume that **the presence of eight electrons in the outermost shell of an atom confers extra stability**. Such a configuration of eight electrons is known as **octet configuration**. This explains the inability of the inert gases to combine with other atoms.

Cause of Chemical Combination

Other elements do not have octet configuration. They tend to achieve the octet configuration of the inert gases by gaining or losing appropriate number of electrons. It is this tendency on the part of the elements to attain the noble gas electronic configuration that causes chemical combination.

Modes of Combination

The chemical combination between two atoms takes place either by the transfer of electrons from one atom to another or by sharing

of lectrons between them. This is the basis of chemical combination. Thus, **the combination of two or more atoms by the redistribution of electrons (by transfer or sharing) between themselves so that all of them achieve the stable inert gas electronic configuration of minimum energy, is called chemical bonding.**

Types of Chemical Bonds

1. Electrovalent or Ionic Bond.
2. Covalent Bond.
3. Co-ordinate Bond.

Electrovalent Bonds—Electrovalent bonds are formed by the complete transfer of one or more electrons from one atom to another.

Let us consider the formation of sodium chloride molecule. Sodium atom has the electronic configuration $1s^2\, 2s^2\, 3p^6\, 3s^1$. The outermost shell contains only one electron. Sodium atom loses one electron to attain a very stable electron configuration ($1s^2\, 2s^2\, 2p^6$) like the nearest inert gas, neon.

$$Na \rightarrow Na^+ + e$$
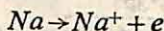
Chlorine atom has the electronic configuration $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^5$. It requires only one electron to achieve a stable inert gas configuration of argon ($1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6$). By gaining an electron Cl becomes chloride ion (Cl^-),

$$Cl + e \rightarrow Cl^-$$
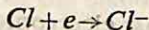
When sodium and chlorine react together the outer electron of sodium is transferred to the chlorine atom to produce Na^+ and Cl^- ions. These oppositely charged ions are now held together by the electrostatic attraction. Na^+Cl^- is now formed.

$$Na \overset{x}{} + \cdot \ddot{\underset{..}{C}}l : \longrightarrow Na^+ \left[\overset{x}{\underset{..}{\ddot{C}}}l : \right]^- \text{ Or } Na^+ Cl^-$$
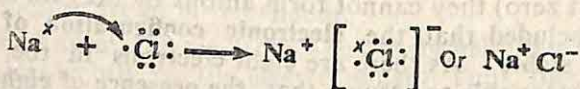
The process is energetically favourable, as both the atoms attain a very stable inert gas configuration.

Calcium atom may lose two electrons to two chlorine atoms forming a Ca^{++} and two Cl^- ions.

Ca(20) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, \vdots 4s^2$ valence electrons

Cl(17) $1s^2\, 2s^2\, 2p^6\, \vdots 3s^2\, 3p^5$ valence electrons

$$Ca : \overset{\longrightarrow \cdot \ddot{C}l :}{\underset{\longrightarrow \cdot \ddot{C}l :}{}} \longrightarrow Ca^{++} \quad \begin{matrix} : \ddot{\overline{C}}l : \\ \\ : \ddot{\overline{C}}l : \end{matrix} \quad \text{or } Ca^{++} 2Cl^-$$
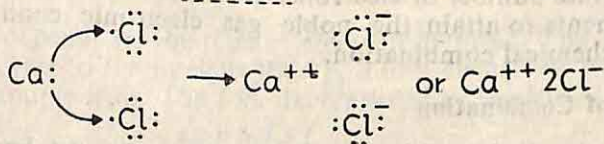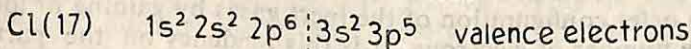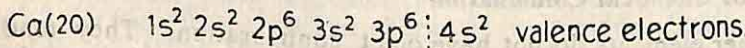
A few other electrovalent compounds are formulated below :

Calcium bromide $(CaBr_2)$

$$Ca\!: \ + \ 2\cdot\ddot{\underset{..}{Br}}\!: \longrightarrow \left[Ca\right]^{++} 2\left[:\ddot{\underset{..}{Br}}\!:\right]^{-}$$

Sodium monoxide (Na_2O)
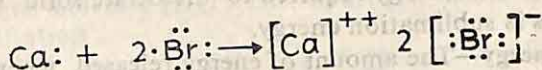
$$\begin{matrix} Na^{\bullet} \\ \ \\ + \ \ddot{\underset{..}{O}}: \\ \ \\ Na^{\bullet} \end{matrix} \longrightarrow \begin{matrix} Na^{+} \\ \ \\ Na^{+} \end{matrix} \left[:\ddot{\underset{..}{O}}:\right]^{--} \ \text{or} \ Na_2^{++}O^{--}$$
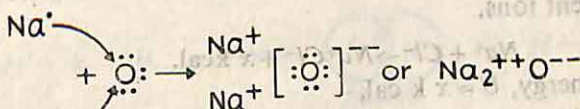
Calcium sulphide (CaS)

$$Ca^{x}_{x} \ + \ \ddot{\underset{..}{S}}: \longrightarrow Ca^{++} \left[\overset{x}{\underset{x}{\ddot{S}}}:\right]^{=} \ \text{or} \ Ca^{++}S^{--}$$
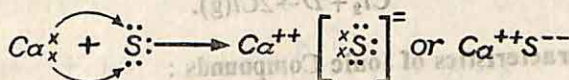
The electrovalent compounds exist as composed of positive and negative ions. They are also referred to as **Ionic Compounds.**

Ionic bonds are formed when electropositive elements combine with electronegative elements.

The compounds formed by the combination of metals of group II A and II A with non-metals of groups V A, VI A and VII A are electrovalent compounds (or ionic compounds).

Energy Changes in the Formation of an Ionic Compound

$$\begin{cases} Na(s) \xrightarrow{\ S\ } Na(g) \\ \tfrac{1}{2}Cl_2(g) \xrightarrow{\ \tfrac{1}{2}D\ } Cl(g) \end{cases}$$

$$-\Delta H_f \qquad \xrightarrow{\ -U\ } \begin{cases} Na^{+}(g) \\ Cl^{-}(g) \end{cases} \xrightarrow{\ -E\ }$$

$$Na^{+}Cl^{-}(s)$$

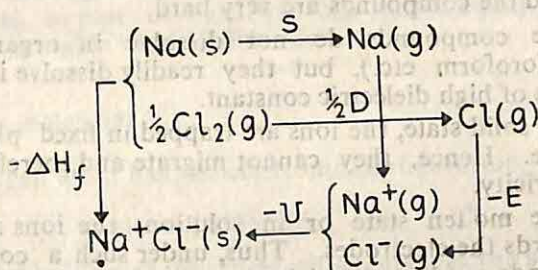Total heat change (ΔH_f) involved in the formation of one mole of $Na^{+}Cl^{-}$ crystal from solid Na and gaseous Cl_2 does not depend upon the steps involved. Hence, from Hess's law,

$$-\Delta H_f = S + \tfrac{1}{2}D + I - E - U$$

S = sublimation energy,
D = Dissociation energy,
I = Ionization potential,
E = Electron affinity, and
U = lattice energy.

Sublimation Energy—Sublimation is conversion of a solid to a gas. The amount of energy required to dissociate solid sodium into sodium atoms is sublimation energy.

Lattice Energy—The amount of energy released when one mole of gaseous negative and positive ions are brought together into a crystal is called the lattice energy or crystal energy. Higher the lattice energy, greater is the electrostatic force of attraction between the constituent ions.

$$Na^+ + Cl^- \rightarrow Na^+Cl^- + x \text{ kcal.}$$
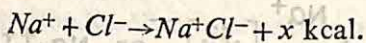
Lattice energy, $U = x$ k cal.

Dissociation Energy—This is the amount of energy required to dissociate a chlorine molecule (Cl_2) into free atoms.

$$Cl_2 + D \rightarrow 2Cl(g).$$
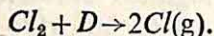
General Characteristics of Ionic Compounds :

(i) An x-ray examination of such compounds has revealed that these compounds are made up of ions, not molecules, even in the solid state.

The ions are arranged together in a regular way in the lattice.

(ii) The attraction between the ions is electrostatic and non-directional. It extends equally in all directions. Thus, to melt the ionic compound the lattice has to be broken. This requires large energy. Hence, the melting point and the boiling point are usually very high, and the compounds are very hard.

(iii) These compounds do not dissolve in organic solvents (benzene, chloroform etc.), but they readily dissolve in water and other solvents of high dielectric constant.

(iv) In the solid state, the ions are trapped in fixed places in the crystal lattice. Hence, they cannot migrate and therefore cannot conduct electricity.

(v) In the mo1ten state or in solution, the ions are free and migrate towards the electrodes. Thus, under such a condition the ionic compounds conduct electricity.

(vi) Ionic reactions are usually very rapid.

The Covalent Bond

Lewis suggested that the formation of non-ionic compounds takes place as a result of sharing of electrons between atoms whereby each atom attains a noble gas configuration (i.e. either 2 electrons as in *He* or 8 in the outermost shell, as in other noble gases). Thus, a bond or force holding atoms together through sharing of electrons is known as a covalent bond. The compounds formed in this way are called covalent compounds. Some of the examples of covalent

compounds are given below :

(i) **Hydrogen molecule (H_2)** : The hydrogen atom has the electronic configuration :

$$H(1) \qquad 1s^1 \qquad \text{or} \qquad H\cdot$$
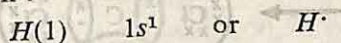
H represent the nucleus and the dot the one valence electron. The combination of two such atoms can be shown as,

$$H\cdot \ + \ \cdot H \ \longrightarrow \ \left(H \ {\large\textcircled{\!:\!}} \ H \right) \quad \text{Or} \quad H-H$$
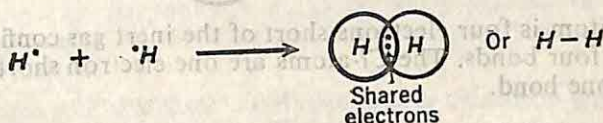
Shared
electrons

(ii) **Hydrogen fluoride molecule (HF)** :

$$H\cdot \ + \ \cdot \ddot{\underset{..}{F}}\cdot \ \longrightarrow \ \left(H \ {:} \ \ddot{\underset{..}{F}}{:} \right) \quad \text{or} \quad H-\ddot{\underset{..}{F}}{:}$$
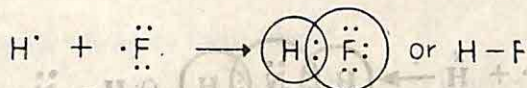
(iii) **Chlorine molecule (Cl_2)** :

$$:\ddot{\underset{..}{Cl}}\cdot \ + \ \cdot \ddot{\underset{..}{Cl}}: \ \longrightarrow \ \left(:\ddot{\underset{..}{Cl}} \ {\large\textcircled{\!:\!}} \ \ddot{\underset{..}{Cl}}: \right) \quad \text{Or} \quad Cl-Cl$$
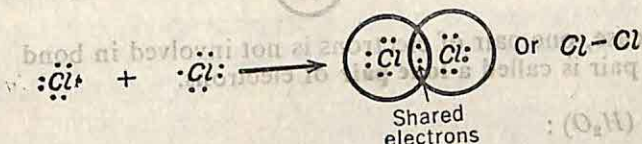
Shared
electrons

Each Cl atom gives a share of one of its electrons to the other atom. Thus, a pair of electrons are shared equally between the two atoms. A stable octet is thus formed.

(iv) **Oxygen molecule (O_2)** :

The oxygen atom has the electronic configuration,

$$O(8) \qquad 1S^2 2S^2 2p^4 \qquad \text{or} \qquad :\ddot{O}:$$
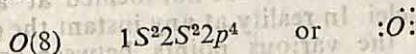
The combination of two such atoms involves the sharing of two pairs of electrons between them.

$$\overset{x\,x}{\underset{x\,x}{O}}{}^{x}_{x} \ + \ :\ddot{O}: \ \longrightarrow \ \left(\overset{x\,x}{\underset{x\,x}{O}} \ {\large\textcircled{\!:\!}} \ \ddot{O}: \right) \quad \text{Or} \quad O=O$$
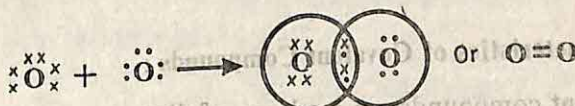
(v) **Carbon tetrachloride ($C\,Cl_4$)** :

A molecule of carbon tetrachloride is made up of one carbon and four chlorine atoms.
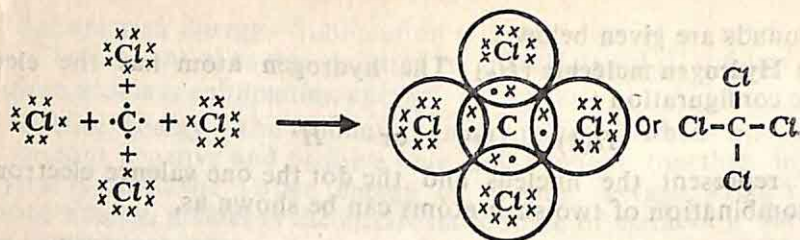
The C atom is four electrons short of the inert gas configuration, so it forms four bonds. The Cl-atoms are one electron short, so they each form one bond.

(vi) Ammonia (NH_3) :

A molecule of ammonia is made up of one nitrogen and three hydrogen atoms.
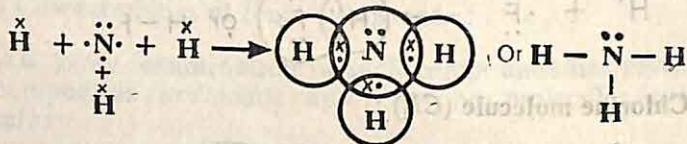
In this case, one pair of electrons is not involved in bond formation. This pair is called a **lone pair** of electrons.

(vii) Water (H_2O) :
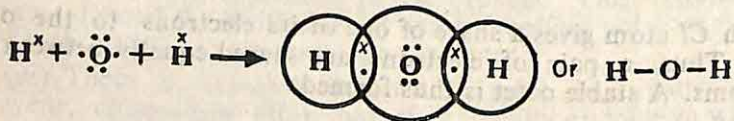
In water molecule (H_2O) there are two lone pairs.

It must be mentioned here that the shared pair or pairs of electrons forming covalent bond are not located at a fixed position between the two nuclei. In reality at any instant the electrons may be located at any of the various points between or around the two nuclei. However, there is a much greater probability of finding the electrons between the two nuclei than at the far ends of the molecule.

General Characteristics of Covalent Compounds :

(i) Covalent compounds are made up of discrete molecules, not of ions.

(ii) The covalent bonds are directional. The binding forces existing between the atoms in a covalent molecule are strong.

(iii) In the solid, the forces between the molecules are the weak van der Waals forces. Hence, the energy needed to melt or boil the compound is small. Thus, the melting point and the boiling point of such compounds are usually low, and these compounds are often gases, liquids or soft solids.

(iv) In molten state or in aqueous solution these compounds do not dissociate into ions, hence the covalent compounds are non-conductors of electricity.

(v) Covalent compounds are not normally soluble in water but are readily soluble in organic solvents (benzene, carbon tetrachloride, chloroform etc.).
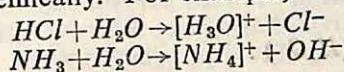
But some of these compounds are highly soluble in water because they react with it chemically. For example,

$$HCl + H_2O \rightarrow [H_3O]^+ + Cl^-$$
$$NH_3 + H_2O \rightarrow [NH_4]^+ + OH^-$$

The Co-ordinate Bond or Dative Bond :

The co-ordinate bond is a special type of covalent bond in which the pair of sharing electrons comes originally from one atom only. Such a bond is called a **co-ordinate bond**.

A co-ordinate bond is represented by an arrow to distinguish it from a two-electron single bond. For example, in the compound $BF_3.NH_3$ both the electrons come from NH_3.

$$\text{H:N: + B:F} \longrightarrow \text{H:N: B:F} \quad or \quad H_3N \rightarrow BF_3$$
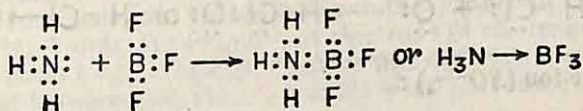
Once a co-ordinate bond is formed it becomes indistinguishable from normal covalent bonds. Hence, the use of arrow to indicate a co-ordinate bond has now been dropped and a single covalent bond is used instead, i.e.,

$$F-B---N-H$$
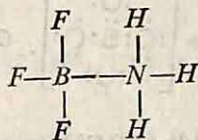
Other examples of co-ordinate bond are given below :

(ii) Ammonium ion (NH_4^+) :

$$\text{H:N: + H}^+ \rightarrow \left[\text{H:N:H} \right]^+ \quad or \quad \left[H-N \rightarrow H \right]^+$$

In NH_4^+ ion there are three covalent and one co-ordinate bond. But once the co-ordinate bond is formed it cannot be distinguished from the other three covalent bonds. Hence, all the four bonds have been shown in the same way.

(iii) Sulphur dioxide (SO_2) and Sulphur trioxide (SO_3) :

$$\ddot{\underset{..}{O}}: + :\ddot{S}: + \ddot{\underset{..}{O}}: \longrightarrow \ddot{\underset{..}{O}}::S:\ddot{\underset{..}{O}}: \text{ or } O=S\rightarrow O$$

$$\ddot{\underset{..}{O}}: + :\ddot{\underset{+}{S}}: + \ddot{\underset{..}{O}}: \longrightarrow \ddot{\underset{..}{O}}::S:\ddot{\underset{..}{O}}: \text{ or } O=S\rightarrow O$$
$$:\underset{..}{\overset{..}{O}}: \qquad\qquad \underset{..}{\overset{\downarrow}{O}}$$

(iv) Hydronium ion, (H_3O^+) :

$$H-\ddot{\underset{..}{O}}: + H^+ \longrightarrow \left[H-\ddot{\underset{H}{O}}:H \right]^+ \text{ or } \left[H-\underset{H}{O}\rightarrow H \right]^+$$
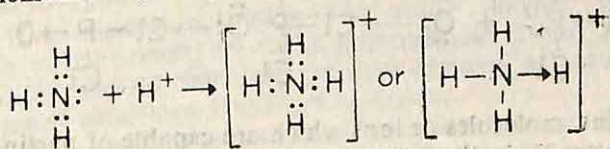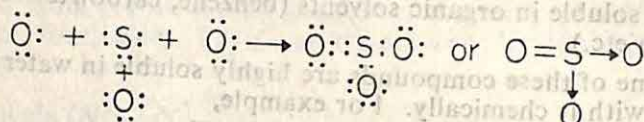
(v) Hypochlorous acid, ($HClO$) :

$$H:\ddot{\underset{..}{Cl}}: + \ddot{\underset{..}{O}}: \longrightarrow H:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{O}}: \text{ or } H-Cl\rightarrow O$$

(vi) Sulphate ion (SO^{--}_4) :

$$:\ddot{S}: + 2e \longrightarrow \left[:\ddot{\underset{..}{S}}: \right]^{--}$$

$$\left[:\ddot{\underset{..}{S}}: \right]^{--} + 4\ \ddot{\underset{..}{O}}: \longrightarrow \left[\begin{matrix} :\ddot{O}: \\ :\ddot{O}:\ddot{S}:\ddot{O}: \\ :\ddot{O}: \end{matrix} \right]^{--} \text{ or } \left[\begin{matrix} O \\ \uparrow \\ O\leftarrow S\rightarrow O \\ \downarrow \\ O \end{matrix} \right]^{--}$$

(vii) Phosphorous Oxychloride ($POCl_3$) :

$$\begin{matrix} Cl \\ | \\ Cl-P: \\ | \\ Cl \end{matrix} + \ddot{\underset{..}{O}}: \longrightarrow \begin{matrix} Cl \\ | \\ Cl-P:\ddot{\underset{..}{O}}: \\ | \\ Cl \end{matrix} \longrightarrow \begin{matrix} Cl \\ | \\ Cl-P\rightarrow O \\ | \\ Cl \end{matrix}$$

The atoms, molecules or ions which are capable of parting off a pair of electrons in the formation of a co-ordinate bond are called **donors**, whereas those which can accept it are called **acceptors**.

## General Characteristics of Co-ordinate Compounds :

(i) The co-ordinate bond is rigid and directional, and hence it may show space isomerism.

(ii) These compounds sparingly dissolve in water but dissolve readily in organic solvents.

(iii) In the molten or in aqueous solution, these compounds do not dissociate into ions. Hence, they are non-conductors of electricity.

(iv) The m. p. and b. p. lie in between ionic and covalent compounds.

Generally, compounds formed between atoms of the same element are non-polar covalent, but the compound having a co-ordinate bond develops polarity. For example, O_2 is non-polar covalent but O_3 is polar.
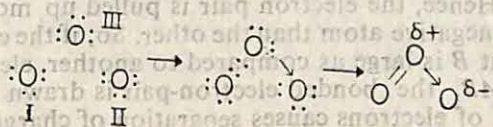
Double Bond and Triple Bond :

There are a number of compounds in which more than two electrons (one pair) are shared between two atoms in the formation of covalent bonds. If two pairs of electrons (4 electrons) are shared, a double bond (=) is formed. If three pairs of electrons (6 electrons) are shared between two atoms, a triple bond (≡) is formed.

Ethylene
(Double bond)

$$H : C :: C : H \quad \text{or} \quad H—C \equiv C—H$$
Acetylene (triple bond)
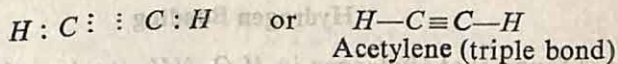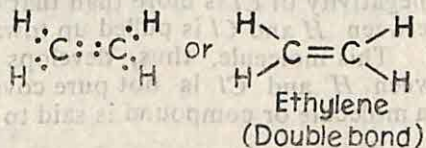
Polarity in Covalent Compounds :

on the basis of nuclear composition the molecules can be classified into two groups :

(i) **Homonuclear molecules**—The atoms having similar composition of their nuclei are called homonuclear atoms. The molecules formed by the combination of homonuclear atoms are known as homonuclear molecules, i.e., H_2, Cl_2, O_2 etc.

(ii) **Heteronuclear molecules**—The atoms having different composition of their nuclei are called heteronuclear atoms. The molecules formed by the combination of heteronuclear atoms are known as heteronuclear molecules, i.e., HF, HCl, HBr, NH_3 etc.

In the formation of a covalent bond between homonuclear atoms, the shared electrons are symmetrically distributed in the molecule, because the electronegativity of both the atoms are the same.

$$H^{\cdot} + {}^{\cdot}H \rightarrow H : H$$

$$\ddot{O}: + :\ddot{O} \rightarrow \ddot{O} :: \ddot{O}$$
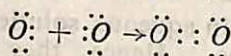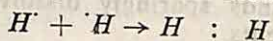
The shared electrons occupy position exactly in between the two atoms, without showing any preference to either of the atoms. In such molecules the centre of positive charge coincides with the centre of negative charge. Hence, the molecules do not develop any charge and are, therefore, neutral. The compounds are **non-polar covalent,** and the bonds are purely covalents.

In heteronuclear molecules one atom is more electronegative than the other. Hence, the electron pair is pulled up more towards the more electronegative atom than the other. So, if the electro-negativity of an element B is large as compared to another element A in the compound AB, the bonded electron-pair is drawn more towards B and this pull of electrons causes separation of charge as follows :

$$A : B \rightarrow \overset{\delta+}{A} \rightarrow \overset{\delta-}{B} \quad \text{or,} \quad \overset{\delta+}{A} - \overset{\delta-}{B}$$

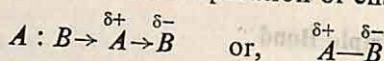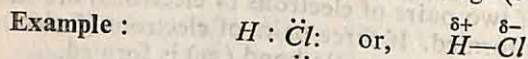A develops a small amount of positive charge ($\delta+$), whereas B develops a small amount of negative charge ($\delta-$).

Example : $H : \ddot{C}l:$ or, $\overset{\delta+}{H} - \overset{\delta-}{Cl}$

The electro-negativity of Cl is more than that of H. Hence, the electron-pair between H and Cl is pulled up towards Cl much more than towards H. This molecule, thus, develops dipole as shown. The bond between H and Cl is not pure covalent, it is partially covalent. Such a molecule or compound is said to be **polar covalent.**

Hydrogen Bonding

It is found that Hydrogen in H_2O, NH_3 etc. has the tendency to form weak linkage. Because of charge-separation in these molecules H acquires a small positive charge while the other partner is left with a small negative charge.

$$\overset{\delta+}{H} - \overset{\delta-}{O}$$
$$|$$
$$\underset{\delta+}{H}$$
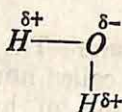
The positive end of one molecule attracts the negative end of the other. In this way a number of molecules get associated to form a bigger aggregate.

The hydrogen bonding in hydrogen fluoride may be depicted as,

$$(.. \overset{\delta+}{H} - \overset{\delta-}{F} .. \overset{\delta+}{H} - \overset{\delta-}{F} .. \overset{\delta+}{H} - \overset{\delta-}{F} .. \overset{\delta+}{H} - \overset{\delta-}{F} ..)_x$$
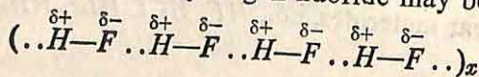
Thus, it is seen in both water and hydrogen fluoride that H atom is bonded to the electro-negative atom by a covalent bond in a single molecule, but by electrostatic force to the electronegative atom in an adjacent molecule. Hydrogen atom, thus, serves as a bridge between two O atoms (in H_2O) and two F atoms (in HF).

Hydrogen bond is thus an electrostatic force of attraction which binds hydrogen of one molecule with the electro-negative atom of another molecule of the same substance.

The electrostatic force or the Hydrogen bond is, however, very much weaker than the covalent bond.

It is due to Hydrogen Bonding that some substances have unusually high boiling points. For example, H_2S, in which there is no hydrogen bonding, is a gas, while H_2O, in which appreciable hydrogen bonding is present, is a liquid (B.P. $= 100°C$) at the ordinary temperature.

Failures of the Octet Theory :

The octet rule satisfies the formation of a large number of compounds, but it fails in the following cases :

(i) According to the octet rule, an atom can hold neither more than 8 nor less than 8 electrons in its outermost shell to achieve stability. But in the formation of several compounds this rule breaks down, i.e.,

:Cl: Be : Cl: :Cl: B : Cl:

(4 bonding electron)   (6 bonding electron)

        :Cl:

:Cl: Al : Cl:

(6 bonding electron)

:Cl: :Cl: :F: :F:

:Cl: P :Cl: :F: S :F:

:Cl: :F: :F:

(10 bonding electron)   (12 bonding electron)
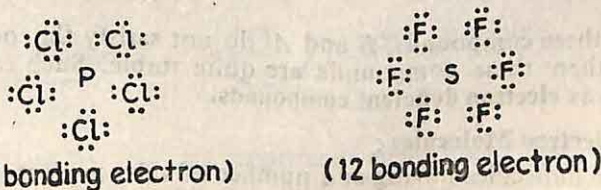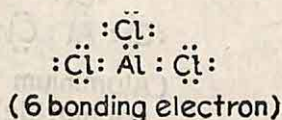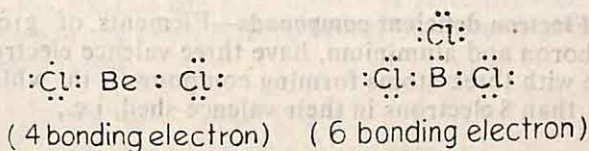
(ii) **Delocalised Bonding**—It is the common knowledge that two

electrons can hold only two atoms. But in case of H_3^+ two electrons hold three atoms together.

$$\left[H \!-\! \begin{matrix} H \\ H \end{matrix} \right]^+ \longleftrightarrow \left[H \begin{matrix} \\ H \\ H \end{matrix} \right]^+ \longleftrightarrow \left[H \quad \begin{matrix} H \\ H \end{matrix} \right]^+$$
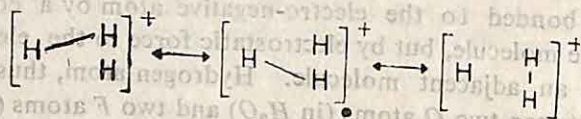
In such a case, the bonding between the H atoms is not stationary rather it is resonating between them as shown. Such a bond holding different atoms together is known as a **delocalised bonding.**

(iii) **Concept of Singlet Linkage**—In order to explain the formation of PCl_5 and SF_6 **Sudgen** suggested the idea of **singlet linkage.** It was assumed that some of the halogen atoms are attached to the central atom by the sharing of one electron only. The linkage thus formed is known as a **singlet linkage.** Thus, the structures of PCl_5 and SF_6 can be shown as,
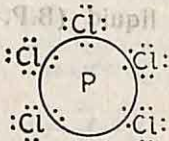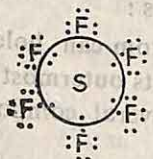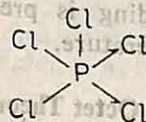
(iv) **Electron deficient compounds**—Elements of group III, particularly boron and aluminium, have three valence electrons. So, they combine with three atoms forming compounds in which they contain less than 8 electrons in their valence shell, i.e.,
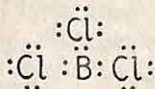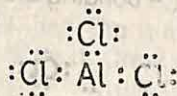
(Boron trichloride)   (Aluminium trichloride)

In these compounds, B and Al do not satisfy the octet rule, but even then these compounds are quite stable. Such compounds are known as **electron deficient compounds.**

Odd Electron Molecules :

The molecules having odd number of valence electrons are called odd electron molecules.

Examples : (i) He_2^+

$$[He : He]^+$$

(ii) **Nitric oxide** (NO)—In this molecule the total number of valence electrons is $5+6=11$.

$$N \equiv\!\!\!=\!\!\!= O\; \cdot\cdot$$

(iii) **Chlorine dioxide** (ClO_2) :

Total number of valence electrons $= 7+2\times6 = 19$.

$$\ddot{\underset{..}{Cl}} :\cdot\cdot \ddot{\underset{..}{O}} :$$
$$\searrow \;\; \ddot{\underset{..}{O}} :$$
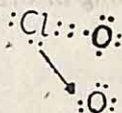
The Orbital Theory of Covalent Bond

What is an Orbital ?

The region in the three-dimensional space in which the probability of finding the electron is the highest is called an **Orbital**.

Overlapping of Orbitals—In the formation of a bond orbitals of two atoms occupy a portion of each other's orbital. This phenomenon is called **overlapping of orbitals.**

Let us consider the idea of electron-sharing in terms of orbitals. When two $1s$ orbitals (say), each possessing one electron, occupy different regions in space, sharing of electrons would not occur, i.e., no bond between the two can be formed. A bond between them is possible only when the two electrons **occupy the same region in space** and have **opposite spins.**
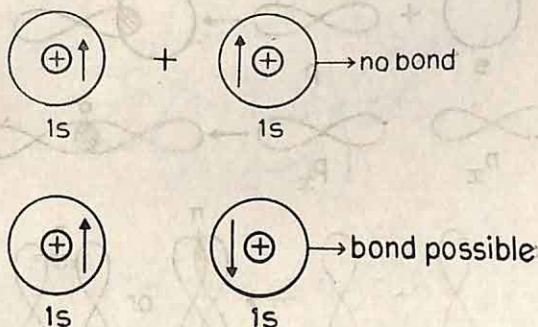
When the two $1s$ orbitals approach each other, the potential energy of the system gradually falls. When the potential energy

reaches a minimum value, the two s-orbitals overlap.
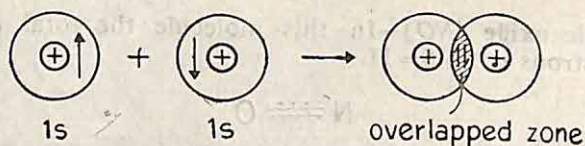
The two electrons now occupy a common region in space (over-lapped zone).   A covalent bond is thus, formed.

The larger the overlapping of orbitals, the stronger is the bond formed.

Sigma (σ) and Pi (π) bonds :

A bond is formed by the overlap of atomic orbitals.

When two half-filled atomic orbitals overlap along the same axis, the bond formed is called a sigma bond.

When two half-filled atomic orbitals overlap laterally or sidewise, the bond formed is called a pi bond.

Thus,   s-s overlapping gives a σ-bond.
                         s-p   ,,   ,,   ,,
On the contrary, p_x-p_x ,,   ,,   ,,
                 p_y-p_y ,,   ,,   π-bond
                 p_z-p_z ,,   ,,   ,,
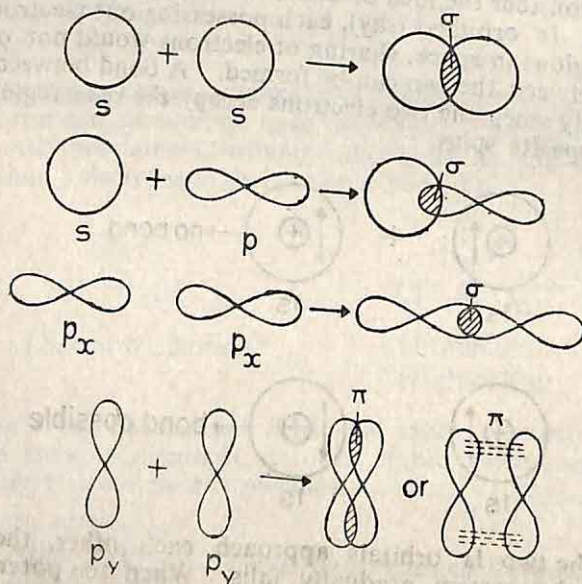
The sigma bond is always stronger than pi bond.

(i) **Hydrogen Molecule** (H_2)—The formation of Hydrogen mole-cule by overlapping of two $1s$ orbitals takes place as shown above. The paired electrons in the overlapped zone have opposite spins.

(ii) **Fluorine Molecule** (F_2)—A fluorine atom has the following configuration :

$$F(9) \quad 1s^2\,2s^2\,2p^5$$
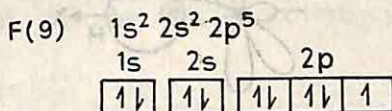
One of the $2p$ orbitals is only half-filled. The two F atoms may combine each other through the overlap of the two half-filled orbi-tals. This may be shown as :

overlapping
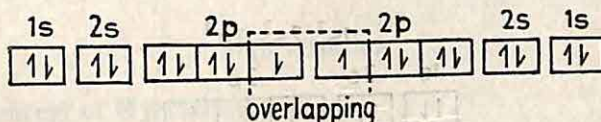
A single bond is thus formed between two F atoms by the sha-ring of pair of electrons. Each F atom acquires 8 electrons which is the maximum capacity of the four orbitals with $n=2$. The bond is p-p bonding.
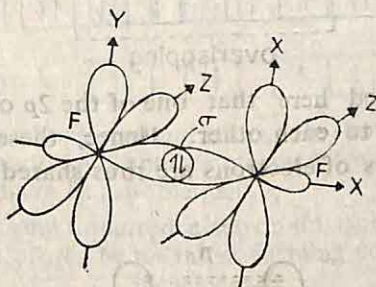
(iii) **Formation of HF Molecule**—$1s$ orbital of Hydrogen can accommodate one electron more. The F atom can also complete its octet by sharing its unpaired electron with that of H atom. The overlap takes place between the $1s$ orbital of H atom and the $2p$

orbital of F atom.
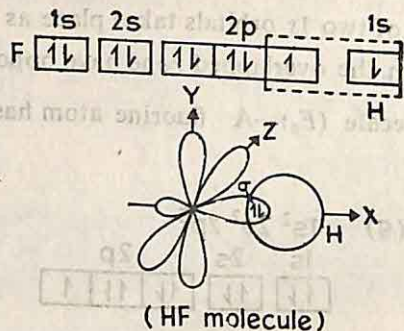
(HF molecule)

The bond between H and F atoms is called **s-p** bonding.

(iv) **Formation of Oxygen Molecule (O_2)**—The O-atom has the following electronic configuration :

$$1s^2 \, 2s^2 \, 2p^4$$
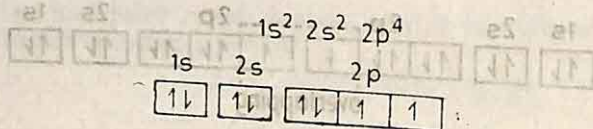
There are, thus, two unpaired electrons occupying the two $2p$ orbitals. Thus, the two $2p$ orbitals of one atom overlap with that of another atom.

overlapping
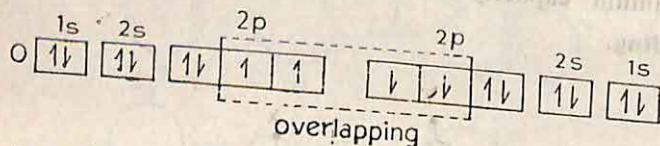
It is to be noted here that one of the $2p$ orbitals of both the atoms are parallel to each other. Hence, these orbitals overlap sidewise. Two pairs of electrons are thus shared forming a **Double bond.**
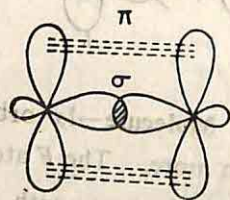
(v) **Formation of Nitrogen Molecule (N_2)**—The N atom has the

following electronic configuration :

N(7) $1s^2 2s^2 2p^3$

1s	2s	2p		
↑↓	↑↓	↑	↑	↑
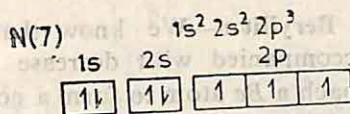
In this case, the union between two atoms of N takes place by the overlapping of three pairs of orbitals. One pair overlaps along the same axis, while the other two pairs overlap sidewise.

	1s	2s	2p			2p			2s	1s	
N	↑↓	↑↓	↑	↑	↑	↓	↓	↓	↑↓	↑↓	N

←- - - - overlapping - - - - →
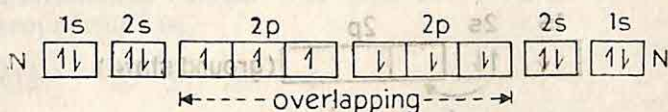
Three electron-pair are thus shared forming a **triple bond** in the molecule. One of these bonds is a sigma (σ) bond, while the other two are pi (π) bonds.

Hybridisation

Why the Concept of Hybridisation ?

To answer this question, let us look at the electronic configuration of **Beryllium, Boron** and **Carbon.**

	1s	2s	2p		
Be (4)	↑↓	↑↓			
B (5)	↑↓	↑↓	↑		
C (6)	↑↓	↑↓	↑	↑	
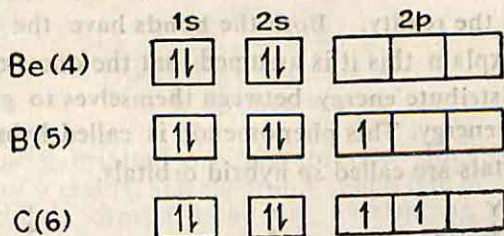
According to the above configurations, Be should be **zero-valent,** as it does not contain any unpaired electron (or half-filled orbital). Be should, thus, behave as a noble gas.

Boron atom has one unpaired electron in one of its p-orbitals and it should, therefore, be **univalent** forming compounds like BH, BCl etc.

Carbon atom has two unpaired electrons in two of its p-orbitals. Carbon should, therefore, be **divalent** forming compounds like CH_2, CCl_2 etc.

But we all know that Beryllium exhibits divalency and Boron trivalency in all their compounds. Similarly, Carbon has always been found to display tetravalency in its compounds.

In order to explain such anomalies the concept of **hybridisation** was provoked.

Hybridisation in Beryllium—We know that the formation of a covalent bond is accompanied with decrease of energy. When reacting atoms approach a *Be* atom to form a covalent bond, some energy is released. This energy is supposed to excite-one of its $2s$ electrons into a vacant *p*-orbitals. This condition of the atom is said to be an **excited state**. The electronic configuration of *Be* (4) now changes as follows :
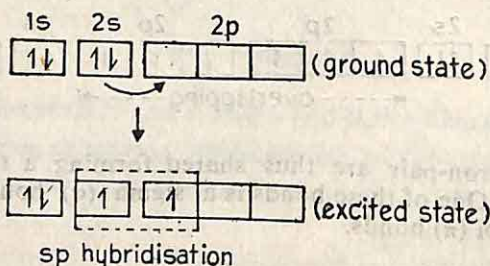
In the excited state *Be* has two unpaired electrons. It is now capable of forming two covalent bonds. It actually does so in compounds like BeH_2 and $BeCl_2$.

But we know that $2s$ and $2p$ orbitals have different energies. Hence, the two bonds should be of different strengths. This is, however, not the reality. Both the bonds have the same strength. In order to explain this it is assumed that the one *s* and one *p* orbital of *Be* redistribute energy between themselves to give two orbitals of equivalent energy. This phenomenon is called **hybridisation**. The two new orbitals are called *sp* hybrid orbitals.
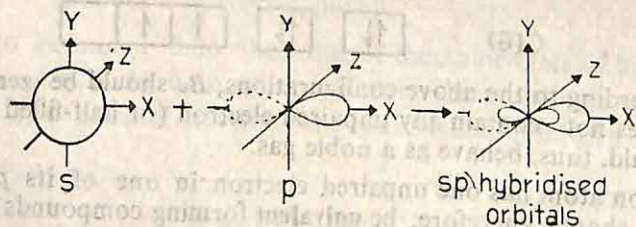
The formation of BeF_2 may now be easily described.

$$F(9) \qquad 1s^2\, 2s^2\, 2p^2_x\, 2p^2_y\, 2p^1_z$$
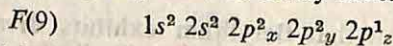
One of the *p*-orbitals is only half-filled. This half-filled orbital

of each F atom overlaps with one Sp hybrid orbital. Thus, BeF_2 is formed.

Two sp hybrid orbitals + F atom = BeF_2
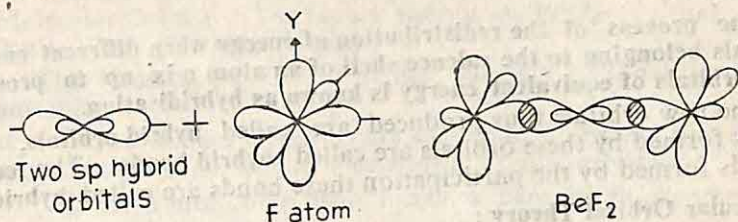
Hybridisation in Carbon—The electronic configuration of Carbon in the ground state is,

C (6) $1s^2\ 2s^2\ 2p^2$

1s   2s   2p   (ground state)
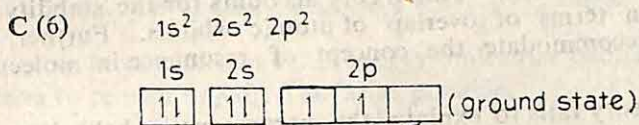
The presence of two unpaired electrons shows that Carbon should behave as a divalent element. But the tetravalency of Carbon is undoubtedly well established. So, in order to explain the tetravalency of Carbon it is assumed that one of its $2s$ electrons is promoted or excited to the vacant $2p$ orbital. The four orbitals (one $2s$ and three $2p$) now hybridise to produce four sp^3 hybridised orbitals of equivalent energy. This is known as sp^3 hybridisation.

2s   2p
sp^3 hybridised
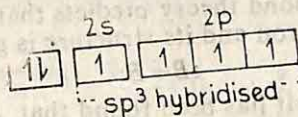
The four sp^3 hybridised orbitals are now directed towards the four corners of a regular tetrahedron. Each one of these four sp^3 hybridised orbitals forms a bond by overlapping with $1s$ orbital of the H atom.

methane (CH_4)
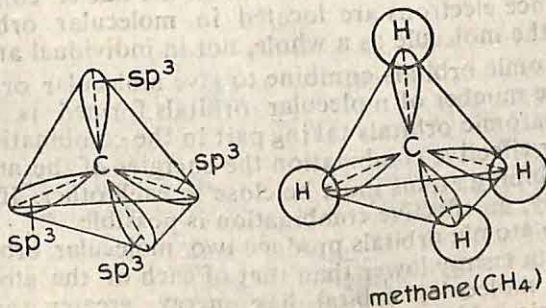
Considering the above case, we may now define **hybridisation** as follows :

The process of the redistribution of energy when different energy orbitals belonging to the valence shell of an atom mix up to produce new orbitals of equivalent energy is known as hybridisation.

The new orbitals thus produced are called **hybrid orbitals,** and bonds formed by these orbitals are called **hybrid bonds.** The compounds formed by the participation these bonds are called **hybrids.**

Molecular Orbital Theory :

In the valence bond theory, the molecule is regarded as made of atoms which retain their individual identity to some extent even when chemically bonded. This theory accounts for the stability of a molecule in terms of overlap of atomic orbitals. Further, the theory can accommodate the concept of resonance in molecules like SO_2.

But the theory fails to explain the paramagnetic behaviour of Oxygen molecule. In the light of the V.B. theory, the structure of O_2 is represented as,

$$:\ddot{O} = \ddot{O}:$$

The structure involves an overlap of two p-orbitals of the two oxygen atoms to form a sigma (σ) bond and an overlap of the two other p-orbitals to form a π bond. In this structure, the molecule does not contain any unpaired electron. But it has been found that O_2 molecule is paramagnetic and contains two unpaired electrons.

Similarly, valence bond theory predicts that B_2 molecule should have no unpaired electron and its structure is given as,

$$:B - B:$$

But experimentally it has been found that B_2 molecule contains two unpaired electrons.

The defects in the valence bond theory have largely been met through the introduction of **Molecular Orbital** concept. The basic approach of the molecular orbital theory is : (i) the valence electrons are considered to be associated with all the nuclei concerned. That is, the valence electrons are located in molecular orbitals, characteristic of the molecule as a whole, not in individual atomic orbitals.

(ii) Atomic orbitals combine to give molecular orbitals.

(iii) The number of molecular orbitals formed is equal to the number of atomic orbitals taking part in the combination.

(iv) For effective combination the energies of the atomic orbitals of the combining atoms must be close to each other. If their energies differ widely, no effective combination is possible.

(v) Two atomic orbitals produce two molecular orbitals, one of which has an energy lower than that of each of the atomic orbitals. The other molecular orbital has energy greater than the higher energy atomic orbital.

The molecular orbital having lower energy is called **Bonding Molecular Orbital**. The higher energy molecular orbital is called **Antibonding Molecular Orbital**.

The bonding M. O. is stable, whereas antibonding M. O. is unstable.

(vi) The valence electrons are distributed among the molecular orbital in the same way as electrons in atomic orbitals.

(vii) Each molecular orbital has a capacity to accommodate a maximum of two electrons.

(viii) Electrons are filled up in M.O.'s in the order of increasing energy. Lower energy M.O.'s are filled up first.

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2p_x} < \pi_{2p_y} = \pi_{2p_z} < \pi^*_{2p_y} = \pi^*_{2p_z}$$

(ix) In case of two equal energy molecular orbitals, the electrons tend to remain unpaired as far as possible.

Examples :

(i) H_2 **Molecule**—Total electrons $= 2$.
Bond order or Number of bonds

$$= \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1$$

Thus, in H_2 there is a **single bond**.

(ii) He_2 **Molecule**—Total electrons $= 4$.

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2 - 2}{2} = 0.$$

∴ He_2 molecule cannot exist, i.e., two He atoms cannot combine to form a He_2 molecule.

(iii) O_2 **Molecule**—Total electrons $= 16$.
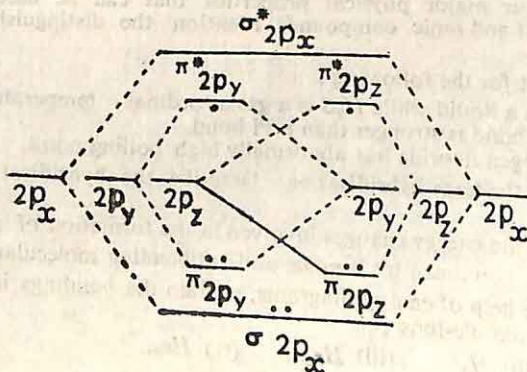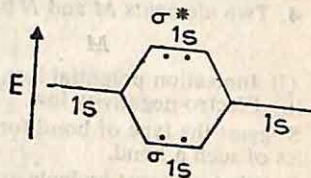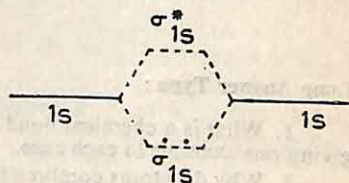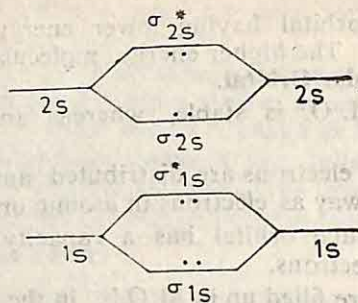
Molecular configuration :

$$\sigma^2_{1s} \; \sigma^{*2}_{1s} \; \sigma^2_{2s} \; \sigma^{*2}_{2s} \; \sigma^2_{2p_x} \; \pi^2_{2p_y} \; \pi^2_{2p_z} \; \pi^{*1}_{2p_y} \; \pi^{*1}_{2p_z}$$
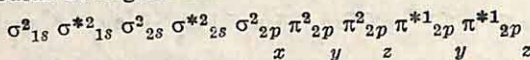
Bond order $= \dfrac{N_b - N_a}{2} = \dfrac{10 - 6}{2} = 2.$

Number of unpaired electrons $= 2$.

$\therefore \quad O_2$ molecule is paramagnetic.

Questions

Long Answer Type :

1. What is a chemical bond ? Define clearly the three types of bonding, giving one example in each case.

2. Why do atoms combine to give molecules ? Give examples.

3. Account for the chemical inactivity of the noble gases.

4. Two elements M and N have the following characteristics ;

M	N
(i) Ionisation potential low.	(i) Ionisation potential high.
(ii) Electro-negativity low.	(ii) Electro-negativity high.

Suggest the type of bond formed when M and N combine. Give four characteristics of such a bond.

5. What is meant by **ionic** and **covalent** bonds ? How would you differentiate an ionic bond from that of a covalent bond ?

6. State four major physical properties that can be used to distinguish between covalent and ionic compounds. Mention the distinguishing features in each case.   (IIT 1978)

7. Account for the following :

(i) H_2O is a liquid while H_2S is a gas at ordinary temperature.   (IIT 1978)

(ii) Sigma bond is stronger than a Pi bond.

(iii) Hydrogen fluoride has abnormally high boiling point.

8. Explain the term **hybridisation**. Describe the hybridisation involved in case of Carbon.

9. Discuss the energy changes involved in the formation of ionic compounds.

10. What do you mean by **bonding** and **antibonding** molecular orbitals ?

11. With the help of energy diagrams, explain the bondings in the following molecules and molecule-ions :

(i) H_2,   (ii) H_2^+,   (iii) He_2^+,   (iv) He_2.

12. Explain why

(i) O_2 molecule is paramagnetic,
(ii) F_2 molecule is diamagnetic,
(iii) He is mono-atomic.

13. What is meant by bond order ? Calculate the bond order of He_2^+, O_2, N_2, H_2^+, and H_2 molecules.

Short Answer Type :

1. Define an ionic bond.
2. Explain the nature of co-ordinate bond.
3. Clearly explain what do you mean by a stable electronic configuration.
4. Indicate the nature of bonds in the following compounds :

(i) CH_3Cl, Cl_2, NH_3, K_2O, CH_3OH, CaH_2 **(IIT 1966)**
(ii) CO_2, H_2O, CaO, CH_4, N_2, SO_4^{--}, Al_2O_3, NH_4^+, CaC_2, $NaCl$, H_2S
                                                        (IIT 1969)
(iii) Cl_2O, CCl_4, Mg_3N_2, NaI, C_2H_2 **(IIT 1971)**
(iv) ClO_4^-, $MgCl_2$ **(IIT 1975)**
(v) MgF_2, $BrCl$, CBr_4, C_2N_2. CuS, PH_3 **(IIT 1978)**

[Solution : (i) Ionic : K_2O, CaH_2
     Covalent : CH_3Cl, Cl_2, NH_3, CH_3OH
(ii) Ionic : CaO, CaC_2, $NaCl$
     Covalent : CO_2, H_2O, CH_4, N_2, SO_4^{--}, Al_2O_3, NH_4^+, H_2S
(iii) Ionic : Mg_3N_2, NaI
     Covalent : Cl_2O, CCl_4, C_2H_2
(iv) Ionic : $MgCl_2$
     Covalent : ClO_4^-
(v) Ionic : MgF_2, Cus
     Covalent : $BrCl$, CBr_4, C_2N_2, PH_3]

5. Give the Lewis dot structure for the following :

(i) IO_3^-,   (ii) N_2O_4,   (iii) SO_2Cl_2,   (iv) $P_2O_7^{-4}$ **(IIT 1978)**

Answer :

(i) $\left[\ddot{\underset{\ddots}{O}} : I : \ddot{\underset{\ddots}{O}} \right]^-$ (with $:\ddot{O}:$ above)

(ii) $:\ddot{O}: N : N :\ddot{O}:$ (with $:\ddot{O}$ and $\ddot{O}:$ below)

(iii) $:\ddot{Cl} : \ddot{S} : \ddot{Cl} :$ (with $:\ddot{O}:$ above and $:\ddot{O}:$ below)

(iv) $\left[:\ddot{O}:\ddot{P}:\ddot{O}:\ddot{P}:\ddot{O}: \right]^{-4}$ (with $:\ddot{O}:$ above and $:\ddot{O}:$ below)
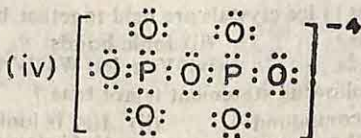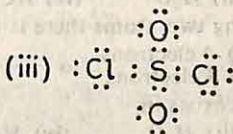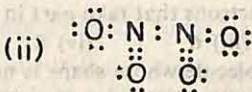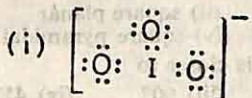
6. What is hydrogen bond ?
7. What do you mean by the overlapping of orbitals ?

8. Distinguish between sigma and Pi bonds.
9. Explain why the maximum covalency of Sulphur is six.
10. What is lattice energy ?
11. What is difference between atomic and molecular orbitals ?
12. Give the number of electrons that could occupy bonding in H_2^+, H_2 and He_2.

Objective Questions

(A) 1. Which of the following is an electrovalent compound ?
(i) CH_3OH (ii) $C_6H_{12}O_6$ (iii) CH_4 (iv) $BaCl_2$

2. When pure CCl_4 or $CHCl_3$ is added to a solution of $AgNO_3$, then which of the following is obtained ?
(i) white precipitate of $AgCl$,
(ii) white precipitate of $AgCl$ soluble in excess of CCl_4 or $CHCl_3$,
(iii) no precipitate is obtained,
(iv) precipitate soluble in excess of $AgNO_3$ is obtained.

3. Which among the following is a good conductor of electricity in the solid state ?
(i) Camphor   (ii) Bauxite   (iii) Graphite   (iv) Sodium Chloride.

4. Which one of the following compounds has an electrovalent linkage ?
(i) $BaCl_2$ (ii) C_2H_6 (iii) SO_2 (iv) NH_3.

5. The electro-negativity values of elements A and B are 0·9 and 3·0 respectively. The bond formed between A and B would be
(i) covalent bond   (ii) Ionic bond
(iii) co-ordinate bond   (iv) triple bond.

6 Element A is strongly electropositive and element B is strongly electronegative. Both are univalent. The compound formed would be
(i) A^+B^- (ii) A^-B^+ (iii) $A-B$ (iv) $A{\to}B$.

7. Which of the following is covalent ?
(i) H_2 (ii) CaO (iii) KCl (iv) Na_2S.

8. The shape of CCl_4 is
(i) linear   (ii) square planar
(iii) tetrahedral   (iv) square pyramidal.

9. The bond angle in H_2S is closer to
(i) 100°   (ii) 120°   (iii) 90°   (iv) 45°.

10. The total number of electrons that take part in forming the bond in N_2 is
(i) 2   (ii) 4   (iii) 6   (iv) 8.

11. Of the following, the molecule whose shape is not linear is
(i) CO_2 (ii) CO (iii) H_2O (iv) HCl.

12. In a double bond connecting two atoms there is a sharing of
(i) 2 electrons   (ii) 4 electrons
(iii) 6 electrons   (iv) 8 electrons.

13. Co-ordinate covalent bond exists in
(i) SO_2 (ii) SO_3 (iii) H_2O_2 (iv) H_2O.

14. Water molecules in ice crystals are held together by
(i) covalent bonds   (ii) ionic bonds
(iii) hydrogen bonds   (iv) Van der Waals' forces.

15. Which of the following statement is not true ?
(i) $AlCl_3$ is ionic compound   (ii) AlF_3 is ionic compound
(iii) AgI is covalent compound   (iv) NaI is ionic compound.

16. Methane is an example of
(i) sp hybridisation   (ii) sp^2 hybridisation
(iii) sp^3 hybridisation   (iv) sp^3d^2 hybridisation.

17. Linus Pauling received the Nobel Prize for his work on
  (i) atomic structure   (ii) chemical bonds
  (iii) photosynthesis   (iv) thermodynamics.

18. A polar bond is formed between atoms which have
  (i) similar electro-negativities   (ii) different electro-negativities
  (iii) metallic bonds   (iv) high melting points.

19. Which of the following pairs form an ionic compound
  (i) C and S (ii) S and O (iii) P and Cl
  (iv) C and Cl (v) K and O.

20. The electro-negativity of B is much greater than that of A. When A and B combine, the bond formed between A and B is
  (i) covalent   (ii) polar covalent   (iii) ionic   (iv) co-ordinate.

21. Cl^- ion is formed by the gain of one electron by the Cl atom. The size of Cl^- ion will be
  (i) equal to that of Cl (ii) bigger than that of Cl
  (iii) smaller than that of Cl (iv) none of these.

22. When two atomic orbitals overlap linearly, the bond formed is a
  (i) covalent bond   (ii) sigma bond
  (iii) Pi bond   (iv) Hydrogen bond.

23. Boron trichloride is
  (i) an ionic compound   (ii) co-ordinate compound
  (iii) electron deficient compound (iv) a base.

24. Which one of the following would you expect to form a strongly ionic solution in water ?
  (i) NaI (ii) CCl_4 (iii) O_2 (iv) CO_2.

25. Of the following compounds, the only one that does not contain double or triple bond is
  (i) H_2O (ii) HCN (iii) CO (iv) N_2.

26. Which of the following molecules is formed by an $s-s$ overlapping ?
  (i) HCl,   (ii) Cl_2,   (iii) H_2O,   (iv) H_2,   (v) N_2.

27. In the formation of CH_4 molecule the C atom makes use of
  (i) Sp^3 hybridization,   (ii) Sp^2 hybridization,
  (iii) Sp hybridization,   (iv) dsp^2 hydbridization.

(B) Select the correct statements from the following :

1. Cations are smaller in size than the corresponding atoms.

2. Sigma bond is weaker than a Pi bond.

3. An aqueous solution of $NaCl$ is a good conductor of electricity because it contains ions.

4. The octet theory fails to explain the formation of SF_6.

5. H_2S is a gas because its molecules are held together by hydrogen bonds.

Answers :

(A) **1.** (iv), **2.** (iii), **3.** (iii), **4.** (i), **5.** (ii), **6.** (i), **7.** (i), **8.** (iii), **9.** (iii), **10.** (iii), **11.** (iii), **12.** (ii), **13.** (ii), **14.** (iii), **15.** (i), **16.** (iii), **17.** (ii), **18.** (i), **19.** (v), **20.** (iii), **21.** (ii), **22.** (ii), **23.** (iii), **24.** (i), **25.** (i) **26.** (iv), **27.** (i).

(B) 1,   3,   4.

□ □ □

CHAPTER 3

PERIODIC CLASSIFICATION OF ELEMENTS

When quite a large number of elements became known, it was difficult for the scientists to study them separately. In order to study them systematically and to correlate their properties attempts have been made from time to time to classify them into different classes.

The main advantages of such a classification of elements are :

(i) The general properties of a particular class of elements can be easily predicted.

(ii) With the help of general properties, the specific behaviour of each element can be guessed.

(iii) It becomes convenient to compare one class of elements with another class.

(iv) In the study of modern chemistry, it has provided a very useful device to organise knowledge of the structure of atoms and physical and chemical properties of elements.

(v) It offers an ideal opportunity to find out some of the basic reasons for the chemistry of elements.

Dobereiner's triad : Johann Dobereiner in 1829 classified certain elements into **groups of three called triads**. He showed that in each group the atomic weight of the middle element **is nearly the average of the atomic weights of the other two extremes.**

$$Li(7) \qquad Na(23) \qquad K(39)$$
$$Ca(40) \qquad Sr(88) \qquad Ba(137)$$
$$Cl(35\cdot5) \qquad Br(80) \qquad I(127)$$

This idea of Dobereiner turned out to be accidental, but the search for regularities was stepped up vigorously.

Prout's hypothesis—William Prout of England in 1815 suggested that all elements are condensation products of Hydrogen atoms, because their atomic weights are whole multiples of the atomic weight of Hydrogen,

Accurate measurements of atomic weights proved Prout's hypothesis untenable.

Newland's Law of Octaves—In 1863, John Newland suggested that the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note in an octave of music.

Thus, the idea of periodicity among elements was born.

Amongst the various periodic tables now devised, the one constructed independently by Dimitri Mendeleev in Russia and Lothar Meyer in Germany, is at present most widely accepted.

Mendeleev's Periodic Table

The most convincing and orderly arrangement of elements was first accomplished by Dimitri Mendeleev in 1869. The table of elements which he constructed is now universally known as **Mendeleev's Periodic Table.** This table is based on the **periodic law** which is stated as :

The physical and chemical properties of elements are periodic functions of their atomic weights.

The inert gases were not discovered then, but after their discovery they were accommodated in the table. At certain places in the table gaps were left with the idea that elements, yet undiscovered, will fill these places. Mendeleev confidently predicted the properties of several of these unknown elements. It was really very wonderful that after the discovery of these elements their properties were actually found to be almost the same as predicted by Mendeleev.

The Periodic Table consists of **Groups** and **Periods.** There are in all Nine groups and Seven periods. The vertical columns in the table are called **Groups,** while the horizontal rows are called **Periods.**

Characteristics of Groups :

(i) The elements possessing similar properties have been placed in the same group.

(ii) In a group the valency of the elements is the same. For example, Li, Na and K (group I) have the valency 1.

(iii) The groups were further sub-divided into sub-groups A and B. This was necessitated by the differences of properties of elements. For example, alkali metals (Li, Na, K etc.) and coinage metals (Cu, Ag and Au) though being in the same group I differ widely in properties. Hence, alkali metals were placed in sub-group IA, and coinage metals in sub-group IB.

Characteristics of the Periods :

(i) There is a gradual change in the properties of elements in a given period.

(ii) In a period the valency increases.

$$Li \quad Be \quad B \quad C$$
$$1 \quad 2 \quad 3 \quad 4$$

Merits of the Periodic Table :

(i) **It has facilitated the study of Chemistry.** The advent of the Periodic Table has proved to be a boon for the students of chemistry. The study of a representative element in a group gives us a clear

idea about the behaviour of the remaining elements of the same group.

(ii) **Help in Research Works**—The position of an element in periodic table gives us much insight to forecast its general behaviour with other elements.

(iii) **Discovery of New Elements**—Mendeleev had left vacant places for several of the hitherto undiscovered elements. He had boldly predicted the probable properties of these undiscovered elements. For example, he named the missing elements as **eka-silicon** and **eka-aluminium** and predicted their properties. His predictions were later found to be correct. These two elements were renamed after their discovery and were called Gallium (*Ga*) and Germanium (*Ge*) respectively.

(iv) **Correction of Doubtful Atomic Weights**—At Mendeleeve's time, the methods for the determination of atomic weights were greatly improved. The atomic weights of some of the elements were, however, sufficiently in error. But his sequential arrangement of elements was correct. Modern values of atomic weights show that at least three pairs of elements are out of order by their atomic weights.

(a) Cobalt and Nickel.
(b) Argon and Potassium.
(c) Tellurium and Iodine.

Mendeleev, however, placed these elements in their correct groups according to their chemical properties, disregarding the then values of their atomic weights. He boldly expected that accurate determination of atomic weights would show that tellurium has a smaller atomic weight than iodine. His idea was later indeed found to be correct.

Defects in the Periodic Table

(i) **Position of Hydrogen**—The position of Hydrogen in the periodic table is still controversial. It has been placed in Group IA with the alkali metals as well as in Group VIIA with halogens. This is because Hydrogen shows its behaviour similar to both the alkali metals and the halogens.

In view of its electronic configuration ($1s^1$) its position in group IA along with the alkali metals appears to be justified.

(ii) **Position of Rare-earth Elements**—In the sixth period of the

periodic table there are 14 rare earth elements after Lanthanum (La^{57}) having atomic weights between 138·92 and 174·99. If they are arranged in the increasing order of their atomic weights, the regularity of the periodic table is completely paralysed. All these elements have, therefore, been placed together in the same group IIIA. They are now positioned in a separate horizontal row below the periodic table.

(iii) **A group of three elements placed together in Group VIII**—In group VIII, three elements have been placed together.

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

(iv) **Elements with higher atomic weights have been placed earlier to elements with lower atomic weights**.

The arrangement of elements in the increasing order of atomic weights breaks down at some places.

Examples : (a) **Tellurium** (*Te*) **and Iodine** (*I*)—*Te* with atomic weight 127·61 is placed earlier to *I* with atomic weight 126·92. The order should have been just reverse.

(b) **Argon** (*A*) **and Potassium** (*K*)—Because of its chemical inertness Argon (at. wt. = 39·94) was placed in group zero whereas Potassium (at. wt. = 39·09) has been placed in group I.

(c) **Nickel** (*Ni*) **and Cobalt** (*Co*)—Nickel (at. wt. = 58·6) has been preceded by Cobalt (at. wt. = 58·9) in the periodic table.

(v) **Position of Isotopes**—The isotopes of elements find no place in the periodic table.

Modern Periodic Table

(Long Form of Periodic Table)

When Mendeleev proposed his periodic table, atomic structure was not discovered then. Now, Mendeleev's periodic table has been modified in the light of the structure of atoms. The modified periodic table is called **Long Form of the Periodic Table**.

This is based on the **periodic law** which is stated as follows :

The physical and chemical properties of elements are periodic functions of their atomic numbers.

In other words, when the elements are arranged in the order of their increasing atomic numbers, their physical and chemical properties vary periodically with increasing atomic number.

A model of the **Long Form of the Periodic Table** is depicted in the chart overleaf.

INT. CH.-5

LONG FORM OF THE PERIODIC TABLE

s-Block elements — Representative elements

p-Block elements — Representative elements

Noble gas elements

d-Block elements — Transition elements

Period	Valence shell	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
n=1	1s	1 H																	2 He
n=2	2s2p	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
n=3	3s3p	11 Na	12 Mg											13 Aℓ	14 Si	15 P	16 S	17 Cℓ	18 Ar
n=4	4s3d4p	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
n=5	5s4d5p	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
n=6	6s4f5d6p	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tℓ	82 Pb	83 Bi	84 Po	85 At	86 Rn
n=7	7s5f6d7p	87 Fr	88 Ra	89 †Ac	104 Ku	105 Ha													

* Lanthanide elements

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

f-Block elements

† Actinide elements

90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lw

Transuranic elements

In this periodic table, emphasis has been laid on the periodicity in physical and chemical properties of elements and their compounds. The properties are repeated at regular intervals because similar structures appear at the same interval. A model of the Long Form Periodic Table is given in chart on P. 66.

This form of periodic table consists of 18 vertical columns (Groups) and 7 horizontal rows (Periods). Groups I to VII are sub-divided into sub-groups A and B. In group VIII, there are three elements and group IX consists of inert gases. The IXth group is also called group 0.

Elements belonging to a particular group are similar in chemical properties because of their similar electronic configurations.

Group IA	Electronic Configuration
Li	$1s^2 2s^1$
Na	$1s^2 2s^2 2p^6 3s^1$
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

All atoms in group IA contain one electron in their outermost orbit. Hence, they display similar chemical behaviour.

Arrangement of Elements According to Electronic Configuration :

This Periodic table classifies elements based on their electronic configuration (atomic number). The elements arranged in the order of increasing atomic number, are placed in horizontal rows called **periods**. Periods differ in length. The length varies from 2 elements in the shortest to 32 in the longest.

A new period starts with the first element that has one electron in a new main energy level. The order of filling of the energy sub-shells is :

Subshells	$1s$	$2s2p$	$3s3p$	$4s3d4p$	$5s4d5p$	$6s4f5d6p$	$7s5f6d$ ....
Periods	1	2	3	4	5	6	7

The maximum number of electrons accommodated by each type of sub-level is $s=2$, $p=6$, $d=10$ and $f=14$. Thus, the number of elements in each period can be easily calculated from the number and type of sub-levels being filled.

The **first** period consists of two elements Hydrogen and Helium, as it corresponds to the filling of the first energy level.

The third element Lithium has an electron in the second main energy level, and hence it begins the **second** period in the table. Ne (10) in the ground state has electrons in only the first and second main energy levels. But the next element Sodium (Na^{11}) has one electron in the third main energy level. Hence, the **third period** begins with it.

The second and third periods each correspond to the filling of the $2s2p$ and $3s3p$ sub-levels. Hence, each of them consists of 8 elements.

Fourth period corresponds to the filling of the $4s3d4p$ sub-levels. The third main energy level is not completely filled at the end of the third period, but a new period has begun with the first $4s$ electron (K^{19}). The addition of ten $3d$ electrons elongates the fourth period from 8 to 18 elements.

Fifth period has arrangement $5s4d5p$ similar to the fourth period.

Sixth period corresponds to the filling of the $6s4f5d6p$ sub-levels. The addition of fourteen $4f$ electrons brings in 14 elements which are placed in a separate row at the bottom of the table to avoid excessive width. These fourteen elements starting with Lanthanum are called **Lanthanides.**

Seventh period corresponds to the filling of the electrons in the $7s5f6d7p$ sublevels. The elements of this period constitute the **actinide series.** These have been placed in a separate row at the bottom of the periodic table. The total number of elements to be accomodated in this period depends on the number of new elements to be synthesised, in addition to those now known.

Groups :

The vertical columns of elements in the periodic table are termed as **Groups.** The elements within a group have the most striking chemical similarities. Each group of elements possess a particular number of **valence electrons.** These valence electrons are in the outermost energy levels. They possess higher energy than the s^2p^6 outer electronic configuration of the preceding noble gas. This s^2p^6 outer electronic configuration provides maximum stability. Therefore, the noble gases are chemically inactive.

Elements of a given group have different kernels but the same number of valence electrons. For most elements, the number of valence electrons equals the group number. As an example, the electronic configurations of the alkali metals are given below :

Li (3)	$1s^22s^1$
Na (11)	$1s^22s^22p^63s^1$
K (19)	$1s^22s^22p^63s^23p^64s^1$
Rb (37)	$1s^22s^22p^63s^23p^63d^{10}4s^24p^65s^1$

In all these cases, the number of V. E. $= 1$.

However, there are a few groups (V B through VIII) where some variation in the type of valence electrons is seen, but the total number is the same.

In group IVA and V, for example, the size of the kernel influences the chemical behaviour, and so group similarities are not so pronounced.

Group VIII is a special case. There are three vertical columns within this group.

Group VIII

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

These elements have so many valence electrons. The total number of valence electrons is less important. The chemical behaviour of these elements is controlled by some other factors also. Consequently, horizontal elements as well as vertical elements in the period show chemical similarity. It is therefore, that all nine elements have been put in a single group.

The chemical behaviour of some elements also depends on the type of electrons in the valence shell. On this basis, the elements have been sub-divided into three types. Each of these three types is identified by the kind of differentiating electron in the atomic structures. The differentiating electron is one which does not appear in the structure of atoms of next lowest atomic number.

Li (3) $1s^2 2s^1$ P (15) $1s^2 2s^2 2p^6 3s^2 3p^3$

The differentiating electron in Li is $2s$, while in P it is $3p$.

The elements having s or p differentiating electrons are called **representative elements.** They have only s and p valence electrons. They include all the "A" group elements in the periodic table plus Group II B.

Elements with d differentiating electrons are called **transition elements.** They have s and d valence electrons. They include "B" groups in the table, except IIB.

Elements with f differentiating electrons are called **inner transition elements.** All parts of group IIIB and that given at the bottom of the table are included in this.

Division of Elements into Blocks

The division of elements into Blocks in the periodic table is based on the electronic configurations :

1. s-Block Elements
2. p-Block Elements
3. d-Block Elements
4. f-Block Elements.

s-Block elements—The elements belonging to groups IA, IIA and Helium of the Zero-group are called **s-block elements.** These are so called because their atoms receive the last electron in the s sub-level of their outermost energy shell.

H (1)	$1s^1$	Na (11)	$1s^2 2s^2 2p^6 3s^1$
He (2)	$1s^2$	K (19)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.
Li (3)	$1s^2 2s^1$		

p-Block elements—The elements belonging to Groups IIB, IIIA,

IVA, VA, VIA, VIIA and Zero (except helium) are called **p-block elements**. The atoms of these elements receive the last electron in their p-sublevels.

$$N\ (7) \qquad 1s^2 2s^2 2p^3$$
$$P\ (15) \qquad 1s^2 2s^2 2p^6 3s^2 3p^3$$

d-Block elements—The elements belonging to Groups IB, IIIB, IVB, VB, VIB and VIIB and VIII are called d-block elements. The atoms of these elements have d-sublevels in the penultimate shell empty and hence, the last electron enters into these d sublevels. The elements from Sc to Zn in the fourth period, from Y to Cd in the fifth period and from La to Hg in the sixth period are d-block elements.

f-Block elements—The elements in which the last electron enters the f-sublevels of the their atoms are called **f-block elements**. The 14 lanthanides and 14 actinides (from Th to Lw) are f-block elements.

The cause of periodicity in properties is the recurrence of similar outer electronic configurations at definite regular intervals.

Position of Elements in the Periodic Table

The position of elements in the periodic table can be determined from the electronic configurations.

```
Number of Orbits = Number of Period
```

The number of electrons in the last and last but one orbit determines the group number.

Example :

Find out the positions of the following elements in the periodic table :

(i) Na_{11}^{23} and (ii) Cu_{29}^{63}

Solution :

(i) Na_{11}^{23} has the following electronic configuration :

$$1s^2\ 2s^2\ 2p^6\ 3s^1$$

Number of orbits = 3.

∴   Period = 3.

Number of electrons in the last orbit = 1.

All preceding orbits are completely filled.

Hence, group is IA.

(ii) $\mathcal{C}_{29}^{63}$ has the electronic configuration :

$$1s^2 \; 2s^2 2p^6 \; 3s^2 3p^6 3d^{10} 4s^1$$
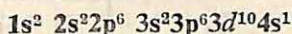
Number of orbits $= 4$.

$\therefore$ Period $= 4$.

Number of electrons in the last orbit $= 1$.

As d-electrons are also involved, the group is IB.

Atomic Properties of Elements

Some of the properties of elements vary periodically with atomic number. These properties are directly related to the electronic configuration of elements. There are other properties like density, melting point etc. which are only indirectly connected to the electronic configuration.

1. **Valency**—The valency is the combining capacity of an element. The valencies of the representative elements (s and p block elements of groups I A to VII A) are generally expressed by x or $(8-x)$, where x is the group number.

Group	I A	II A	III A	IV A	V A	VI A	VII A
Examples	HCl	$BeCl_2$	BCl_3	CH_4	NH_3	H_2O	HF
	H_2O	$CaCl_2$	Al_2O_3	CO_2	PCl_3	H_2S	HCl
	$NaCl$	CaO		SiO_2	PCl_5	SF_6	Cl_2O_7

The number of electrons in the outermost orbit of an atom determines the valency of the element. Hence, these electrons are referred to as the **valence electrons**.

Valency $=$ Number of valence electrons

or,

Valency $= (8 -$ Number of valence electrons).

2. **Atomic size or Atomic radius**—It is difficult to determine the actual size of an atom. However, by knowing the distances between atoms in molecules, the approximate size of atoms can be determined.

Atomic radius increases in going from top to bottom in a group of the periodic table. This is due to the presence of increasing number of electron shells. It is true that nuclear charge also increases, but its effect is small as compared to the effect of a new shell of electrons being added. The underlying electrons in the inner shells shield the outermost electron from the nucleus.

At. No.	Element	Atomic radius (Å)
3	Li	1·23
11	Na	1·57
19	K	2·03
37	Rb	2·16
55	Cs	2·35

Atomic radius decreases in going from left to right in a period of the periodic table. This is due to the effect of the increasing nuclear charge, while the extra electrons are being added to the same shell. With the increased nuclear charge the electron shells are pulled in to a greater extent. The atomic radius is therefore, decreased.

At. No.	3	4	5	6	7	8	9
Element	Li	Be	B	C	N	O	F
Atomic radius (Å)	1·23	0·89	0·80	0·77	0·74	0·74	0·72

3. **Ionisation Potential**—The energy required to remove the most loosely bound electron from the outermost orbit of an isolated gaseous atom, is called the ionisation potential.

$$Na(g) + energy \rightarrow Na^+(g) + e$$
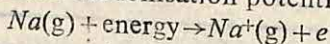
This is also known as the First Ionisation Potential.

The energy needed to remove the second electron from a monopositive ion is called Second Ionisation Potential.

$$Na^+(g) + energy \rightarrow Na^{++}(g) + e$$
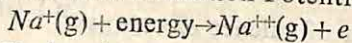
The second I.P. is always greater than the first I.P., as some extra energy has to be applied to overcome the force of attraction due to the positive charge.

The I.P. is usually measured in **electron volt**.

The factors influencing the ionisation potential are :

(i) Atomic size, (ii) Charge on the nucleus, (iii) Screening effect of inner electron shells and (iv) Type of electron involved, (v) Half filled and completely filled orbitals.

(i) In a small atom the electrons are strongly held. In large atoms the electrons are weakly held. The ionisation potential, thus, decreases with increasing size of the atom. Thus, I.P. of K is less than that of Na.

(ii) Charge on the nucleus also affects the value of I.P. The greater the nuclear charge, higher is the value of I.P. Thus, I.P. of Mg is greater than that of Na, partly due to the increased nuclear charge and partly due to the smaller size of Mg. Due to the increased nuclear charge the size of Na^+ is less than a Na atom.

(iii) A valence-shell electron experiences an attractive force with the nucleus and a repulsive force from the inner-shell electrons. The combined effect of these two forces is that the attractive force is weakened. Hence, the ionisation potential decreases.

The weakening of the attractive force due to the presence of inner electron shells between the nucleus and the valence shell electron is known as **screening effect** or **shielding effect**.

Greater the shielding effect, lower is the value of ionisation potential.

(iv) An s electron is much nearer to the nucleus. Hence, it is much more strongly held to the nucleus by the electrostatic force of attraction. It is for this reason that the removal of s electron is difficult as compared to p, d or f electrons. Thus, I.P. decreases in the order :

$$s > p > d > f.$$

(v) **Half filled and completely filled orbitals**—A half filled (ns^1, np^3, nd^5) or completely filled (ns^2, np^6, nd^{10}) orbitals are more stable. Hence, more energy is required to remove them from these orbitals. Thus, the I. P. of an atom having such orbitals is comparatively higher.

The I.P. decreases in moving from top to bottom in a group of the periodic table due to the increased atomic size.

Group I	I.P.
Li	5·39 eV
Na	5·14 ,,
K	4·34 ,,
Rb	4·18 ,,
Cs	3·89 ,,

The I.P. increases in going from left to right in a period of the periodic table due to the decreased atomic size.

Period 3	Na	Mg	Al	Si	P	S	Cl	Ar
First I.P. (eV)	5·1	7·6	6·0	8·2	11·0	10·4	13·0	15·7

The change across a period is not regular because the removal of s electron is more difficult than p or d.

The ionisation potential of an atom varies according to Coulomb's law :

$$E = \frac{q_1 q_2}{r}$$

where, $q_1 =$ charge on an electron,
$\quad\quad q_2 =$ effective nuclear charge
$\quad\quad r =$ average radius of the electron ionised.

The electron ionised is the one for which the energy required is a minimum.

$$E = \frac{e(Z_{eff})}{r}.$$

Thus, the ionisation potential will be lowest when the effective nuclear charge (Z_{eff}) is small and when the average radius of the electron is large.

4. Electron Affinity—The amount of energy released or absorbed when a neutral gaseous atom takes up an electron is called electron affinity.

$$Cl(g) + e \rightarrow Cl^-(g) + \text{Energy}.$$
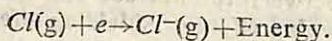
The uninegative ion thus formed repels the addition of further electrons. Hence, energy is required to add on a second electron.

As an example, when an Oxygen atom takes up one electron, energy is released.

$$O + e \rightarrow O^- + 1\cdot 48 \text{ eV}$$
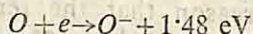
But when an additional electron is added to the O^- ion, a large amount of energy is required to complete the reaction.

$$O^- + e \rightarrow O^{--} - 7\cdot 3 \text{ eV}$$
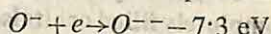
Electron affinity depends on :

(i) size of the atom,
(ii) effective nuclear charge.

The electron affinity decreases as we go down a group in the periodic table. This is because the size of the atom increases and the electron being added goes to higher shells.

Group VIIA	At. No.	Electron affinity (eV)
F	9	3·62
Cl	17	3·79
Br	35	3·56
I	53	3·28

The electron affinity increases as we move from left to right in a period of the Periodic Table. This is because the size of the atom decreases, and the effective nuclear charge increases.

It is found that non-metals have higher electron affinities than metals.

The electron affinity values of elements enable us to predict the relative tendency of elements to gain electrons during chemical reactions.

5. Electronegativity—The electronegativity is defined as the power of the atom in a molecule to attract covalently bonded electron pair towards itself. In contrast to ionisation potential and electron affinity, electronegativity can be considered for elements in any environment, either as free atoms or as parts of molecules.

Electronegativity is a relative value. Generally, small atoms

attract electrons more than large ones and are, therefore, more electronegative.

I. P. and E. A. may be regarded as a measure of electronegativity.

$$\text{Electronegativity} = \frac{\text{I. P.} + \text{E. A.}}{5 \cdot 6}.$$

The values of electronegativities on Pauling's scale are given below :

			H			
			2·1			
Li	Be	B	C	N	O	F
1·0	1·5	2·0	2·5	3·0	3·5	4·0
Na	Mg	Al	Si	P	S	Cl
0·9	1·2	1·5	1·8	2·1	2·5	3·0
K	Ca	Sc	Ge	As	Se	Br
0·8	1·0	1·3	1·7	2·0	2·4	2·8
Rb	Sr		Sn		Te	I
0·8	1·0		1·7		2·1	2·4
Cs	Ba					
0·7	0·9					

The electronegativity increases with increasing number of valence electrons for the metals in groups I, II and III.

Questions

Long Answer Type :

1. Write the periodic law on which Mendeleev's classification of elements is based. Give three defects in Mendeleev's periodic table.

2. What is modern period law ? How have the shortcomings of Mendeleev's periodic table been removed with the adoption of this law as the basis of classification of elements ?

3. Describe the merits of Mendeleeor's periodic table. (M. U. 1978A)

4. Ascertain the position (Group and Period both) of the following elements in the periodic table :

    (a) Magnesium,   (b) Calcium,   (c) Aluminium,   (d) Phosphorus and (e) Oxygen. (R. U. 1971S)

5. What are the basis and utility of the classification of elements into s, p, d and f blocks in the periodic table ? (B. U. 1978A)

6. Write about the modern periodic table and discuss its features. (M. U. 1981A)

7. Account for the general variation in ionisation potential among the elements of a periodic group.

8. Which ion, Co^{++} or Co^{+++}, would you expect to have the smaller radius ? Explain.

9. Account for the following :

    (i) Na^+ is smaller than Na.
    (ii) Cl^- is greater than Cl.
    (iii) First I. P. of Mg is greater than that of both Na and Al.

10. On the basis of electronegativity differences, list the following compounds in the order of increasing ionic character :

    $NaBr$, NaF, CaS, MgO, HF, AlP, CH_4.

Short Answer Type :

1. Differentiate between Mendeleev's periodic table and modern periodic table.

2. An element has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$. What is the position of this element in the periodic table ?

3. Account for the difference in ionisation potential between :
(a) He and Li, (b) Li and Be, (c) Be and B, (d) N and O.

4. Give reasons for the difference in electron affinity between the following pairs of atoms :
(a) O and F
(b) Cl and Br
(c) Cl and F.

5. Which ion is largest in each of the following pairs ?
(i) Na^+ and Mg^{++}
(ii) Mg^{++} and Ca^{++}
(iii) Cl^- and K^+.

6. How is electronegativity of an element related to the ionisation potential and electron affinity ?

7. Define ionisation potential.

8. Mention the factors on which the I. P. of an element depends.

9. State Mendeleev's periodic law.

10. How is ionisation potential related to atomic size ?   (B. U. 1978)

11. How does I. P. of an element vary in a group and period of the periodic table ?   (B. U. 1980)

12. What is a period in a Periodic Table ? How do atomic structures change in a period with increase in atomic numbers from left to right ?

(A) Objective Questions :

1. The vertical columns in the Periodic Table are called
(i) periods (ii) groups (iii) ordinal numbers.

2. The horizontal rows in the Periodic Table are known as
(i) Groups (ii) Periods (iii) Duma's homologous series.

3. The element with atomic number 11 belongs to
(i) First period   (ii) Second period
(iii) Third period   (iv) Fourth period.

4. Sets of elements are given below. Select the set which belongs to alkali metal group.
(i) $Z=2$, 8, 18
(ii) $Z=3$, 11, 19
(iii) $Z=4$, 12, 20
(iv) none of these.

5. The short form of the periodic table was devised by
(i) Dalton (ii) Newlands (iii) Moseley (iv) Mendeleev.

6. The long form of the periodic table was devised by
(i) Rutherford (ii) Moseley (iii) Duma (iv) Thomson.

7. From the following list select the elements which belong to the first group.
(i) $Z=3$, 18, 32   (ii) $Z=12$, 16, 18
(iii) $Z=11$, 19, 37, 55   (iv) $Z=5$, 10, 15, 20.

8. Which of the following is called the coinage metal ?
(i) Cu, (ii) Fe, (iii) Al, (iv) Mg.

9. The law of triad was propounded by
(i) Dobereiner   (ii) Prout
(iii) Newland   (iv) Mendeleev.

10. Diagonal relationship is shown by
    (i) *Li* and *Na*   (ii) *Li* and *Mg*
    (iii) *Be* and *Hg*   (iv) *Zn* and *Cd*.

11. The alkali metals are
    (i) *Li, Na, K*   (ii) *Ca, Sr* and *Ba*
    (iii) *Zn, Cd, Hg*   (iv) *Fe, Co, Ni*.

12. The alkaline earth metals are
    (i) *Li, Na, K*   (ii) *Ca, Sr, Ba*
    (iii) *Zn, Cd, Hg*   (iv) *Fe, Co, Ni*.

13. Outer transition elements are called
    (i) *s* block elements   (ii) *p* block elements
    (iii) *d* block elements   (iv) *f* block elements.

14. The metal which exists as liquid at the ordinary temperature is
    (i) *Na* (ii) *Hg* (iii) *Ag* (iv) *Fe*.

15. The lightest and uninflammable gaseous element is
    (i) *H* (ii) *He* (iii) O_3 (iv) *Ar*.

16. The ionisation potential of elements from top to bottom in a group of the periodic table
    (i) decreases   (ii) increases
    (iii) remains constant   (iv) none of the above.

17. Which of the following elements has lowest value of electronegativity ?
    (i) Sodium   (ii) Chlorine
    (iii) Potassium   (iv) Carbon.

18. Elements whose valency electrons are found to occupy outermost orbitals are called
    (i) *s*-block elements   (ii) *p*-block elements
    (iii) *d*-block elements   (iv) *f*-block elements.

19. Which of the following is the most general property of all the transitional elements ?
    (i)   They are metals
    (ii) They all occur in variable oxidation states
    (iii) All transitional elements are paramagnetic
    (iv) All transitional elements form complexes.

20. Which one of the following is a metalloid ?
    (i) Brass (ii) Mercury (iii) Graphite (iv) Arsenic.

21. Halogen is the name given to family of elements having the outer electronic configuration :
    (i) s^2p^3 (ii) s^2p^4 (iii) s^2p^5 (iv) s^2p^6.

22. Which one of the following elements has the lowest ionisation potential ?
    (i) *F*   (ii) *Cl*   (iii) *Br*   (iv) *I*.

23. Which of the following pairs of elements suggests anomaly in Mendeleev's periodic table ?
    (i) *Be, B*   (ii) *Te, I*   (iii) *Cu, Zn*   (iv) *Ca, Ba*.

24. Which of the following atoms has the largest size ?
    (i) *F*   (ii) *Cl*   (iii) *Br*   (iv) *I*.

25. Which of the following statements is correct ?
    (i)   First I. P. of *Mg* is greater than the first I. P. of *Na*.
    (ii) Second I. P. of *Mg* is greater than the second I. P. of *Na*.
    (iii) First I. P. of *Mg* is equal to the first I. P. of *Na*.
    (iv) Atomic number of elements in a group decreases.

26. Atomic radii is
    (i) half bond length (ii) bond length (iii) the distance between centres of two adjacent atoms (iv) the distance between any two atoms.

27. Non-metals are arranged in a group in
    (i)   ascending order of activity
    (ii) ascending order of electronegativity
    (iii) ascending order of electropositiveness
    (iv) none of the above.   **(PMDT 1977)**

28. Elements towards the left hand of the periodic table
    (i)   tend to be metals
    (ii) have greater tendency to combine with non-metals
    (iii) tend to have lower m. p. than elements at right hand side
    (iv) are always transition metals.   **(PMDT 1977)**

29. The order of reactivity of halogens is
    (i) F, Cl, Br, I (ii) I, Br, Cl, F
    (iii) Br, I, F, Cl (iv) $Cl, Br, I, F.$ **(PMDT 1977)**

30. In the periodic table, elements are arranged in the ascending order of their
    (i)   atomic weights   (ii) atomic volumes
    (iii) atomic numbers   (iv) atomic heats.

31. The most important oxidation state of an element belonging to group VIIA is
    (i) $+1$ (ii) -1 (iii) $+2$ (iv) $-2.$

32. Which of the following is a p-block element ?
    (i) Na (ii) Al (iii) Ca (iv) $Fe.$

33. An element belonging to group VA has
    (i)   5 valence electrons   (ii) 3 valence electrons
    (iii) 8 valence electrons.

34. Which of the following is the fundamental property of the element ?
    (i)   Atomic weight   (ii) Atomic number
    (iii) Atomic volume   (iv) Density.

35. Which of the following has the maximum ionisation potential ?
    (i) Neon   (ii) Calcium   (iii) Potassium   (iv) Magnesium.

(B) Fill up the blanks :

1. The ionisation potential............as we move from left to right in a period of the periodic table.

2. The long form of the periodic table is based on...........

3. The properties of elements with atomic number 10 will resemble the element with atomic number...........

4. In the long form of periodic table, there are vertical columns known as ....and horizontal columns known as...........

5. First period is known as...........period and contains.........elements.

6. Second and third periods are known as...........periods and contain........ elements each.

Ans. A 1. (ii), 2. (ii), 3. (iii), 4. (ii), 5. (iv), 6. (ii), 7. (iii), 8. (i), 9. (i), 10. (ii), 11. (i), 12. (ii), 13. (iii), 14. (ii), 15. (ii), 16. (i), 17. (iii), 18. (i), 19. (i), 20. (iv), 21. (iii), 22. (i), 23. (ii), 24. (iv), 25. (i), 26. (i), 27. (iii), 28. (ii), 29. (i), 30. (iii), 31. (ii), 32. (ii), 33. (i), 34. (ii), 35. (i).

B. 1. increases,   2. atomic number,
   3. 18,   4. groups, periods,
   5. short, two,   6. short, 8.

□ □ □

CHAPTER 4

RADIOACTIVITY

Radioactivity was an accidental discovery in science. Henry Becquerel in 1896, while exploring the properties of X-rays, found that potassium uranyl sulphate could darken a photographic plate in the sunlight or even when wrapped in a black paper. It was thus concluded that a type of radiation was emitted from uranyl salt. This radiation affected a photographic plate and passed through several layers of materials, opaque to ordinary light.

Mme Curie pursued the investigation of such materials and found two new elements, **polonium** and **radium**, which also gave out even more powerful radiations.

The property that certain substances emit a type of radiation which can affect a photographic plate, is called **radioactivity**. Such substances are called **raidoactive**. Thus, Uranium, Polonium and Radium are all radioactive elements.

Types of radiation : The radiation produced by radioactive elements consists of three distinct types :

(i) α-rays : The positively charged rays are called α rays.

(ii) β-rays : The negatively charged rays are called β-rays.

(iii) γ-rays : The rays remaining unaffected by electrical or magnetic fields are called the gamma (γ) rays.

Photographic plate

Radioactive Substance

Properties of α, β and γ rays :
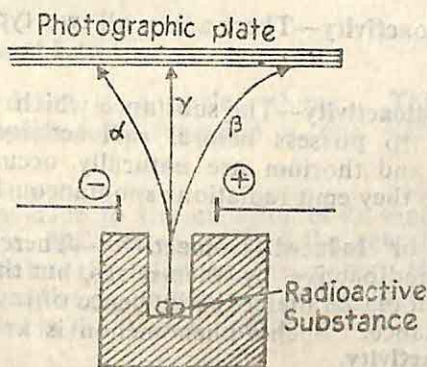
α-rays—(i) The α-rays consist of particles carrying 2 units of positive charge and a mass of 4 units. Thus, α-particles are in reality doubly charged helium atoms (He^{++}).

(ii) The α-rays cause phosphorescence on a Zinc sulphide screen.

(iii) The energies of α-particles range from 4 to 10 Mev, and the velocities from 1.4×10^9 to 2.2×10^9 cm sec^{-1}.

(iv) The α-particles travel in straight lines and when they pass through a gas they knock out some electrons and produce ionised molecules of the gas.

(v) In an electric field, the α-particles are deflected towards the negative pole, indicating that these particles are positively charged.

(vi) The α-particles can penetrate through thin sheets of aluminium. However, they can be stopped by an aluminium foil having thickness of less than 0.1 mm.

β-rays—(i) The β-rays consist of a stream of electrons.

(ii) They travel through gases along much more erratic paths with velocity close to that of light.

(iii) They are about 100 times more penetrating than α-rays.

(iv) In an electric or magnetic field, their direction of deviation shows that they consist of negatively charged particles, identical to electrons.

(v) They possess negligible mass and smaller momentum.

γ-rays—(i) These are massless and uncharged particles and hence remain undeflected in electric or magnetic fields.

(ii) They are electromagnetic radiations of very short wavelengths (between 10^{-8} and 10^{-11} cm).

(iii) γ-rays are extremely penetrating. They are capable of penetrating 100 centimetres thick sheet of aluminium.

(iv) Toxicity—They are harmful to living tissues.

(v) They are weak ionisers of gases.

Types of Radioactivity—There are in all two types of radioactivity :

(i) Natural radioactivity—The substance which emits radiations by itself is said to possess natural radioactivity. For example, uranium, radium and thorium are naturally occurring radioactive elements, because they emit radiations spontaneously.

(ii) Artificial or Induced radioactivity—There are substances which are not radioactive by themselves, but they begin to show radioactivity when placed under the influence of rays from a natural radioactive substance. Such a phenomenon is known as artificial or induced radioactivity.
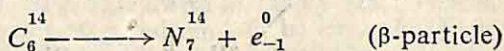
Radioactive Decay :

Radioactivity is a spontaneous decay of the nucleus. During radiation α, β, positron etc. are emitted from the nuclei of radioactive elements.

The effect of decay reactions occurring in natural radioactive substances may be summarised as follows :

(i) α-emission—Loss of an α-particle from the nucleus of an atom decreases its atomic number by two units and its atomic mass by four units.

$$Ac_{89}^{227} \longrightarrow At_{87}^{223} + He_2^4 \quad \text{(α-particle)}$$

$$Ra_{88}^{224} \longrightarrow Rn_{86}^{220} + He_2^4 \quad \text{(α-particle)}$$
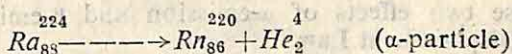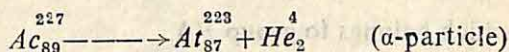
(ii) β-emission—Loss of a β-particle from the nucleus of an atom increases its atomic number by one unit and does not appreciably change its atomic mass.

$$Al_{13}^{28} \longrightarrow Si_{14}^{28} + e_{-1}^0 \quad \text{(β-particle)}$$

$$C_6^{14} \longrightarrow N_7^{14} + e_{-1}^0 \quad \text{(β-particle)}$$
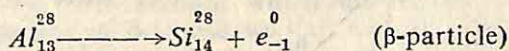
(iii) **Positron-emission**—Loss of a positron from the nucleus of an atom decreases its atomic number by one unit and does not appreciably change its atomic mass.

$$Si_{14}^{27} \longrightarrow Al_{13}^{27} + e_{+1}^0$$
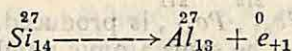
(iv) **Electron-capture**—Capture of an electron by the nucleus of an atom (usually K electron-capture occurs) decreases its atomic number by one unit and does not appreciably change the atomic mass.

$$V_{23}^{49} + e_{-1}^0 \longrightarrow Ti_{22}^{49}$$
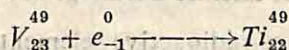
Each of the above nuclear reactions occurs spontaneously.

Group Displacement Law :

Radioactive decay is a nuclear change. This means that as a result of this change, transformation of one element into another takes place.

(i) α-emission—Due to the emission of an α-particle $\left(He_2^4\right)$ from the nucleus of a radioactive element the new element has atomic number two units less than that of the parent element. The new element, thus, occupies a position two groups to the left of that of the parent element in the Periodic table.

For example, Polonium $\left(Po_{84}^{215}\right)$ belongs to group VI A of the periodic table. When it loses an α-particle, it is changed into radioactive lead $\left(Pb_8^{211}\right)$ which is placed in group IV A.

(ii) β-emission—By the emission of a β-particle from the nucleus of a radioactive element the new element formed has atomic number

one unit more than that of the parent element. The new element, thus, goes one place to the right in the periodic table.

For example, radioactive Lead $\left(Pb_{82}^{211}\right)$, an element of group IV A, emits a β-particle and is changed into radioactive Bismuth $\left(Bi_{83}^{211}\right)$ which belongs to group VA.

These two effects of α-emission and β-emission are known as **Group Displacement Law.**

IIIA	IVA	VA	VIA	VIIA

$$Pb_{82}^{211} \xleftarrow{\qquad\alpha\qquad} Po_{84}^{215}$$

$$\downarrow \beta$$

$$Bi_{83}^{211} \xrightarrow{\quad\beta\quad} Po_{84}^{211}$$
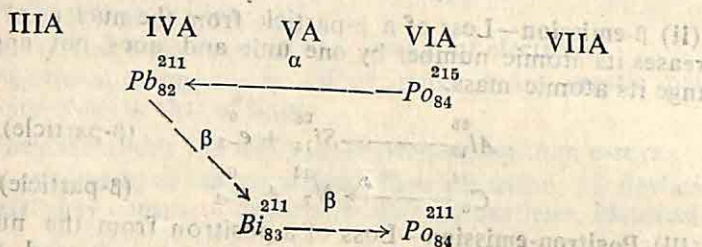
Radioactive Isotopes—As a result of expulsion of one α-particle and two β-particles from Po_{84}^{215}, Po_{84}^{211}, is produced. Po_{84}^{215} and Po_{84}^{211} are isotopes, because they have the same atomic number (84) but different atomic masses (215 and 211).

Rate of Atomic Disintegration

The rate of decay of a radioactive element is independent of temperature and pressure, or any other external factors. In all radioactive disintegrations, it has been found that **the number of atoms disintegrating per unit time is proportional to the number of atoms present** at any instant. Thus,

$$-\frac{dN}{dt} \propto N, \qquad \text{or} \qquad -\frac{dN}{dt} = \lambda N$$

where N is the number of radioactive atoms present at any instant. λ is the proportionality constant, called **disintegration** or **decay constant.** This constant has a characteristic value for a particular radioactive element.

Rearranging the above equation, we get,

$$\frac{dN}{N} = -\lambda dt; \qquad \text{or} \qquad \int \frac{dN}{N} = -\lambda \int dt$$

or

$$\ln N = -\lambda t + C,$$

where C is the constant of integration.

When, $t = 0$, $N = N_0$ (number of atoms initially present).

$$\therefore \ln N_0 = C; \qquad \therefore \ln N = -\lambda t + \ln N_0$$

or $\qquad \ln \dfrac{N}{N_0} = -\lambda t;$ $\qquad$ or $\quad N = N_0\, e^{-\lambda t}.$

Also $\qquad\qquad 2{\cdot}303 \log \dfrac{N}{N_0} = -\lambda t$

or $\qquad\qquad\qquad \log \dfrac{N_0}{N} = \dfrac{\lambda t}{2{\cdot}303}.$

It, thus, follows that radioactive disintegration is an exponential decay process.

Half-life Period—The amount of a radioactive element goes on decreasing with time. The amount which disintegrates per unit time also goes on decreasing. Suppose, we start with 100 g of radium. The half of this amount disintegrates in 1590 years. Hence, at the end of 1590 years, only 50 g radium will be left. In the end of the next 1590 years, the amount of radium left will be only 25 g.

$$100\text{ g} \xrightarrow{\quad 1590\text{ yrs}\quad} 50\text{ g} \xrightarrow{\quad 1590\text{ yrs}\quad} 25\text{ g}$$

This process continues infinitely. The entire amount will never disintegrate completely. The time required for the complete disintegration is infinity, though the amount may become too small to be measured. Hence, in actual practice, the time for complete disintegration does not carry any meaning. Hence, the period taken is the **half-life period**, which is defined as :

The half-life period of a radioactive element is the time required for the disintegration of one-half of the atoms of radioactive species initially present.

Half-life period is a characteristic property of a radioactive species. Different radioactive elements have different half-life periods.

$$\because \quad \log \dfrac{N_0}{N} = \dfrac{\lambda t}{2{\cdot}303},$$

for half-life, $\qquad\qquad N = \tfrac{1}{2}N_0,$

$$\therefore \quad \log \dfrac{2N}{N} = \dfrac{\lambda t_{1/2}}{2{\cdot}303}; \quad (t_{1/2} = \text{half-life period})$$

or $\qquad\qquad \log 2 = \dfrac{\lambda t_{1/2}}{2{\cdot}303}$

or $\qquad\qquad t_{1/2} = \dfrac{2{\cdot}303 \times \log 2}{\lambda} = \dfrac{0{\cdot}693}{\lambda}.$

The half-life period is thus inversely proportional to the

positively charged protons and protons. These attractive forces are known as **Nuclear forces**.

The exact nature of the nuclear forces is not known even today. In 1935, Yukawa, a Japanese physicist, suggested a new type of particle, called **Meson**, which oscillates between nucleons. These mesons interact with protons and neutrons, thereby changing a proton into a neutron, and a neutron into a proton.

$$\text{Proton} + \pi^- \rightleftharpoons \text{Neutron}$$
$$\text{Neutron} + \pi^+ \rightleftharpoons \text{Proton}$$
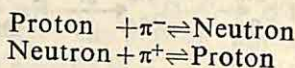
There is, thus, an exchange of meson between neighbouring nucleons. This causes attraction between proton and neutron.

Binding Energy—Binding energy is the energy difference between the actual mass of an atom and mass of its nuclear components (proton, neutron and electron). It is expressed in million electron volts (meV).

$$1 \text{ amu} = 931 \text{ meV}$$

Binding energy per nucleon is the binding energy divided by the number of nucleons present in the nucleus.

Artificial Transmutation of Elements

It is now firmly established that natural radioactive elements can be transmuted or transformed into new elements with the emission of α, or β particles. It was **Rutherford** who first tried the possibility of **artificial transmutation, i.e., the transformation of one element into another by artificial means.**

In 1919, Rutherford reported that the bombardment of nitrogen by α-particles obtained from polonium (a radioactive element) starts a nuclear reaction which can be represented as,

$$N_7^{14} + He_2^4 \longrightarrow H_1^1 + O_8^{17}$$
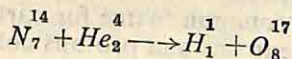
Since then, a large number of transmutations have now been brought about by the bombardment of different elements with particles, such as protons, neutrons, electrons etc. In 1931, Chadwick discovered a chargeless particle, called **neutron** by the bombardment of beryllium with α-particles.

$$Be_4^9 + .He_2^4 \rightarrow C_6^{12} + n_0^1 \quad \text{(neutron)}$$
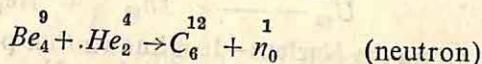
At present, the neutrons have proved to be more useful than α-particles.

Artificial transmutation of historic importance was achieved by I. Joliot and F. Joliot in 1934 who found that when a luminium was bombarded by α-particles, the metal became radioactive due to its

transformation into radioactive phosphorus.

$$Al_{13}^{27} + He_2^4 \rightarrow P_{15}^{30} + n_0^1$$
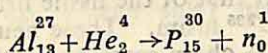
P_{15}^{30} being radioactive itself changes to a stable nuclide Si_{14}^{30}, even if the bombardment is stopped.

$$P_{15}^{30} \rightarrow Si_{14}^{30} + e_{+1}^0 \text{ (positron)}$$
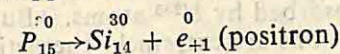
This was the first observed case of **artificial** or **induced radio-activity.**

Some typical examples of artificial transmutation are :

$$Mg_{12}^{24} + He_2^4 \rightarrow Si_{14}^{27} + n_0^1$$
$$\downarrow$$
$$Al_{13}^{27} + e_{+1}^0 \text{ (positron)}$$
$$\text{(stable)}$$

$$B_5^{10} + He_2^4 \rightarrow N_7^{13} + n_0^1$$
$$\downarrow$$
$$C_6^{13} + e_{+1}^0 \text{ (positron)}$$
$$\text{(stable)}$$

$$Li_3^7 + H_1^1 \rightarrow Be_4^8 + \gamma$$
$$\text{(Proton)}$$

$$Na_{11}^{23} + D_1^2 \rightarrow Na_{11}^{24} + H_1^1$$
$$\text{(Deuteron)}$$
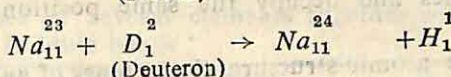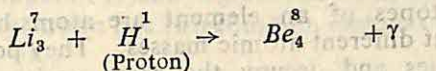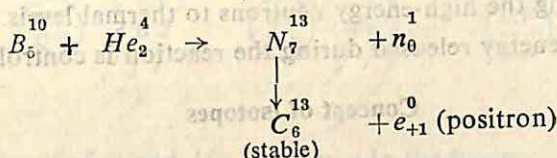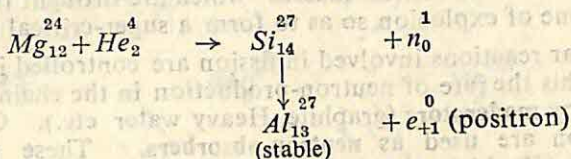
Nuclear Fission :

According to the concept of nuclear binding energy, an appreciable amount of energy is released when very heavy nuclei split into smaller nuclei. For example, bombardment of uranium by neutrons involves at least two sequences of nuclear reactions.
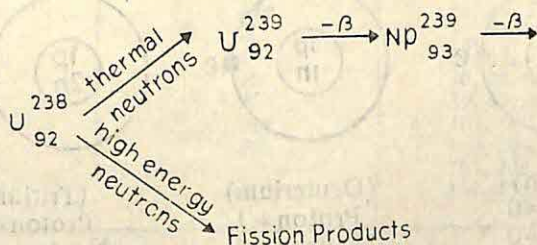
In one of these the uranium-235 isotope absorbs a low-energy neutron and forms a fissionable or unstable nucleus.

$$U_{92}^{235} + n_0^1 \rightarrow U_{92}^{236} \xrightarrow{\text{fission}} n_0^1 + Ba, Kr \text{ etc.} + 200 \text{ MeV}$$
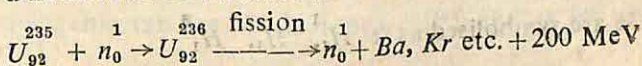
The fission products include a mixture of isotopes whose atomic masses are about half that of the fissile uranium. Three neutrons are produced by each U^{235} atom. These neutrons in turn react with additional U^{235} nuclei. A chain reaction is, thus, started.

The chain continues till the entire amount of U^{235} has reacted.

It is to be noted that only neutrons at thermal energy levels (5 to 10 eV) are absorbed by U^{235} atoms. But the neutrons produced in the fission reactions are extremely energetic. Hence, these high-energy neutrons have to be slowed down. This requires large mass of uranium-235. This is known as the **critical** mass. Any quantity less than this is safe to handle. The Atomic Bomb is, therefore, constructed of two sub-critical masses, which are brought in contact only at the time of explosion so as to form a super-critical mass.

The nuclear reactions involved in fission are controlled in **nuclear reactors**. In this the rate of neutron-production in the chain reaction is controlled by **moderators** (graphite, Heavy water etc.). Cadmium rods or boron are used as **neutron-absorbers**. These neutron-absorbers bring the high-energy neutrons to thermal levels.

Thus, the energy released during the reaction is controlled.

Concept of Isotopes

Definition—The isotopes of an element are atoms having the same atomic number but different atomic masses. They possess the same chemical properties and occupy the same position in the periodic table.

In the light of the atomic structure, the isotopes of an element are atoms whose nuclei contain the same number of protons but different number of neutrons.

Examples : (i) Isotopes of Hydrogen—There are three isotopes of hydrogen : protium, deuterium and tritium.
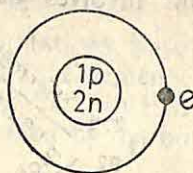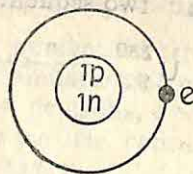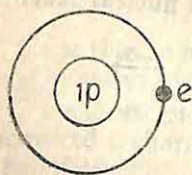
(Protium)
Proton = 0
Neutron = 0
∴ At. No. = 1
At. mass = 1

(Deuterium)
Proton = 1
Neutron = 1
∴ Atomic No. = 1
Atomic Mass = 2

(Tritium)
Proton = 1
Neutron = 2
At. No. = 1
Atomic Mass = 3

These are symbolised as : H_1^1, H_1^2, H_1^3

(ii) **Isotopes of Oxygen**—The three isotopes of oxygen have the same atomic number, i.e., 8 but their atomic masses are 16, 17 and 18.

(iii) **Isotopes of Magnesium**—The three isotopes of Mg have the atomic masses 24, 25 and 26.

$$O^{16} \qquad O^{17} \qquad O^{18}$$

$$Mg^{24} \qquad Mg^{25} \qquad Mg^{26}$$
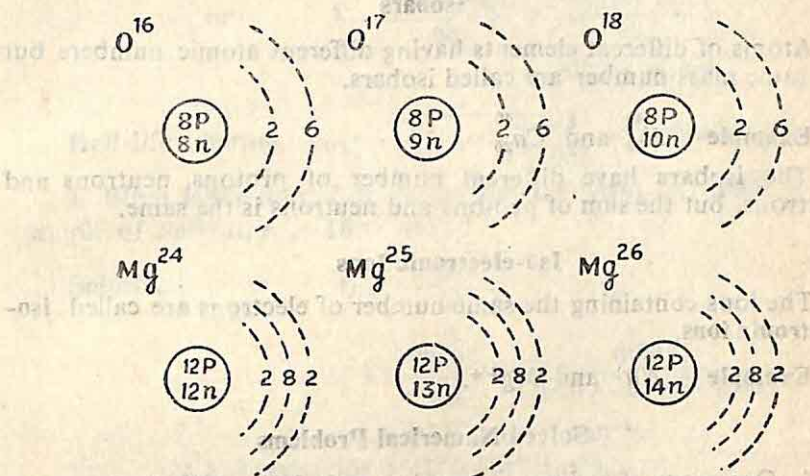
The isotopes of O and Mg are shown in the figure.

Similarly, argon has two common isotopes whose atomic masses are 36 and 40.

Isotopes of several elements together with their atomic masses are given in table below :

Atomic number	Elements	Atomic masses
1	H	1, 2, 3
6	C	12, 13
8	O	16, 17, 18
10	Ne	20, 21, 22
12	Mg	24, 25, 26
16	S	32, 33, 34
17	Cl	35, 37, 39
18	Ar	36, 38, 40
19	K	39, 40, 41
47	Ag	107, 109
82	Pb	203, 204, 205, 206, 207, 208, 209, 210
92	U	234, 235, 238, 239

Fractional Atomic Weight—The fractional atomic weight of an element is due to different proportions of its isotopes present in the element.

For example, chlorine has two isotopes, Cl^{35} and Cl^{37}, in the proportion of 3 : 1.

$$\therefore \text{ Average atomic weight} = \frac{3 \times 35 + 1 \times 37}{4}$$

$$= 35 \cdot 5.$$

Isobars

Atoms of different elements having different atomic numbers but the same mass number are called isobars.

Example : K^{40}_{39} and Ca^{40}_{20}

The isobars have different number of protons, neutrons and electrons, but the sum of protons and neutrons is the same.

Iso-electronic Ions

The ions containing the same number of electrons are called **iso-electronic ions.**

Example : Na^+ and Mg^{++}.

Solved Numerical Problems

1. One gram of radium is found to emit $3 \cdot 70 \times 10^{10}$ particles per second. Calculate the half-life period of radium.

Solution : Number of atoms in 1 g Ra

$$= \frac{6 \cdot 023 \times 10^{23}}{226} = 2 \cdot 66 \times 10^{21} \text{ atoms. } (Ra = 226)$$

Now, $\qquad \because \quad -\dfrac{dN}{N} = \lambda dt$

or $\qquad \lambda = -\dfrac{(dN/dt)}{N}$

$$= \frac{3 \cdot 7 \times 10^{10}}{2 \cdot 66 \times 10^{21}} = 1 \cdot 39 \times 10^{-11} \text{ sec}^{-1},$$

$\therefore$ Half-life, $t_{1/2} = \dfrac{0 \cdot 693}{\lambda} = \dfrac{0 \cdot 693}{1 \cdot 39 \times 10^{-11}}$ sec

$$= 5 \times 10^{10} \text{ sec} = 1580 \text{ years.}$$

2. A radioactive element decays at such a rate that after 68 min, $\frac{1}{4}$th of the original amount remains. Calculate its decay constant and half-life period.

Solution : $\qquad \qquad \lambda t = \ln \dfrac{N_o}{N}.$

After 68 min, $\frac{1}{4}$th of the original amount remains.

So, $\qquad \lambda \times 68 = \ln \dfrac{N_o}{N} = \ln \dfrac{N_o}{N_o/4} = \ln 4$

$\therefore \qquad \lambda \times 68 = 2 \cdot 303 \log 4$

or $\qquad \lambda = \dfrac{2 \cdot 303 \log 4}{68} = \dfrac{2 \cdot 303 \times 0 \cdot 6021}{68}$

$\qquad\qquad\qquad\qquad = 0 \cdot 02038 \text{ min}^{-1}.$

Half-life period, $t_{1/2} = \dfrac{0 \cdot 693}{\lambda} = \dfrac{0 \cdot 693}{0 \cdot 02038} = 34 \cdot 0$ min.

3. What is the rate of disintegration (activity) of $0 \cdot 001$ g of a sample of Ra^{226} if, $t_{1/2} = 1620$ years ?

Solution : $\qquad t_{1/2} = \dfrac{0 \cdot 693}{\lambda}$

$\therefore \qquad \lambda = \dfrac{0 \cdot 693}{t_{1/2}} = \dfrac{0 \cdot 693}{(1620 \times 365 \times 24 \times 60)}$

$\qquad\qquad\qquad = 8 \cdot 137 \times 10^{-10} \text{ min}^{-1}$

$\because \qquad$ 226 g Ra contains $6 \cdot 023 \times 10^{23}$ atoms,

$\therefore \quad 0 \cdot 001$g ,, ,, $\dfrac{6 \cdot 02 \times 10^{23} \times 0 \cdot 001}{226}$ atoms,

$\qquad\qquad\qquad = 2 \cdot 665 \times 10^{18}$ atoms.

Now, $\qquad -\dfrac{dN}{dt} = \lambda N$

$\qquad\qquad\qquad = 8 \cdot 137 \times 10^{-10} \text{min}^{-1} \times 2 \cdot 665 \times 10^{18}$ atoms

$\qquad\qquad\qquad = 2 \cdot 167 \times 10^{9}$ atoms min^{-1}.

4. The half-life period of Radon is $3 \cdot 824$ days. How long would it take for 75% of the sample to disintegrate ?

Solution : $\qquad t_{1/2} = \dfrac{0 \cdot 693}{\lambda}$

$\therefore \qquad \lambda = \dfrac{0 \cdot 693}{t_{1/2}} = \dfrac{0 \cdot 693}{3 \cdot 824 \text{ days}} = 0 \cdot 1811 \text{ day}^{-1}.$

Let N be the number of atoms present at any time t, and N_0 be the number of atoms present initially. Then,

$$2 \cdot 303 \log \dfrac{N_0}{N} = \lambda t$$

Here, $\qquad N_0 = 100$
$\qquad\qquad N = 100 - 75 = 25$

$$\therefore \quad 2\cdot303 \log \frac{100}{25} = 0\cdot1811 \text{ day}^{-1} \times t$$

or $\quad 2\cdot303 \times \log 4 = 0\cdot1811 \text{ day}^{-1} \times t$

or $\quad t = \dfrac{2\cdot303 \times \log 4}{0\cdot1811 \text{ day}^{-1}} = 7\cdot657 \text{ days.}$

5. The half-life period of C^{14} is 5720 years. Calculate the fraction of C^{14} left at the end of 10,000 years.

Solution : $t_{1/2} = \dfrac{0\cdot693}{\lambda}$

$$\therefore \quad \lambda = \frac{0\cdot693}{t_{1/2}} = \frac{0\cdot693}{5720} = 1\cdot212 \times 14^{-4} \text{ year}^{-1}.$$

Now, $\quad 2\cdot303 \log \dfrac{N}{N_0} = -\lambda t$

or $\quad \log \dfrac{N}{N_0} = \dfrac{-\lambda t}{2\cdot303} = \dfrac{-1\cdot212 \times 10^{-4} \text{ year}^{-1} \times 10000 \text{ years}}{2\cdot303}$

$$= -0\cdot5260 = \overline{1}\cdot4740$$

$$\therefore \quad \frac{N}{N_0} = 0\cdot2979.$$

$\therefore$ Fraction left $= 0\cdot2979.$

6. If the atomic weight of a radioactive element is 232 and its atomic number 90, and if it emits six α-particles and 4 β-particles during radioctive disintegration, find the atomic weight and atomic number of the new element.

Solution : Mass of six α-particles $= 6 \times 4 = 24$ units
    Positive charge of six α-particles $= 6 \times 2 = +12$ units
    Mass of 4 β-particles $= 0$
    Negative charge of 4 β-particles $= -4$ units.

$\therefore$ Loss of mass due to emission of both α and β particles $= 24 + 0 = 24$ units

Loss of charge due to emission of both α and β-particles $= +12 - 4 = 8$ units

$\therefore$ Atomic weight of the new element $= 232 - 24 = 208.$
Atomic number of the new element $= 90 - 8 = 82.$

7. From the following nuclear reactions, predict the positions of Po, Mg and C in the periodic table :

(i) $\quad Po_{84}^{210} \rightarrow Pb_{82}^{206} + He_2^4$

(ii) $\overset{27}{Mg_{12}} \rightarrow \overset{27}{Al_{13}} + \overset{0}{e_{-1}}$

(iii) $\overset{14}{C_6} \rightarrow \overset{14}{N_7} + \overset{0}{e_{-1}}$
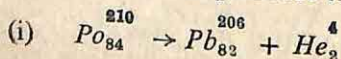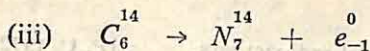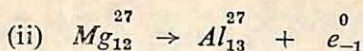
It is known that Pb, Al and N belong to groups IVA, IIIA and VA respectively.

Solution : (i) $\overset{4}{He_2}$ is emitted. As Pb belongs to group IVA, the parent element Po must belong to group VIA.

(ii) In this reaction, a β-particle $\left[\overset{0}{e_{-1}}\right]$ is emitted. It shows that the parent element Mg belongs to group IIA because the daughter element Al belongs to group IIIA.

(iii) In this reaction, a β-particle $\left[\overset{0}{e_{-1}}\right]$ is emitted. It shows that C belongs to group IVA because the new element N belongs to group VA.

8. Calculate the number of alpha and beta particles emitted when radioactive $\overset{232}{Th_{90}}$ changes into $\overset{208}{Pb_{82}}$.

Solution : Change in atomic mass $= 232 - 208 = 24$.

$$\therefore \quad \alpha\left(He_2^4\right) \text{ particles emitted} = \frac{24}{4} = 6.$$

Expected decrease in atomic number due to emission of six α-particles $= 6 \times 2 = 12$

∴ Expected atomic number of the new element $= 90 - 12 = 78$.
But the atomic number of the new element $= 82$.

∴ Increase in atomic number due to emission of β-particles $= 82 - 78 = 4$.

∴ Number of β-particles $= 4$.

Questions

Long Answer Type :

1. What is radioactivity ? How was it discovered ?
2. Discuss two of the properties of α, β and λ rays.
3. Describe Group-displacement law in radioactive elements.
4. What is half-life period ? Prove that the half-life period of a radioactive element is independent of the initial amount.
5. Give a brief account of Natural Radioactivity. What do you know about the characteristic properties of radioactive rays ? How are the atomic numbers and the atomic masses of the parent element affected by the emission of α and β rays ?
(M. U. 1978A)
6. Distinguish between radioactive change and chemical change.
7. Compare alpha (α) and beta (β) particles in respect of their masses and charges. What changes are produced in atomic nuclei by the emission of

these particles ?

Short Answer Type :

1. Write a short note on the discovery of radioactivity.   (P. U. 1972A)
2. What is average life of a radioactive element ?
3. State Group-displacement Law.
4. Define the following terms :
   (i) Nucleon, and (ii) Nuclide.
5. What is transmutation of elements ?
6. What is difference between Natural and Artificial radioactivity ?
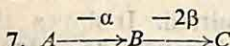
7. $A \xrightarrow{-\alpha} B \xrightarrow{-2\beta} C$
What is relationship between A and C of this equation ?

8. Define 'unit of radioactivity'.

9. From the following nuclear reaction, predict the positions of the two elements in the periodic table :

$$Ta_{73}^{186} \rightarrow W_{74}^{186} + e_{-1}^{0}$$
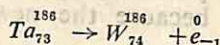
[Ans. Ta belongs to group VA and W to VIA]

10. Name the first and the last element in each of the radioactive disintegration series.

11. Derive the expression, $t_{1/2} = \dfrac{0.693}{\lambda}$, where $t_{1/2}$ and λ stand for half-life period and disintegration constant.

Objective Questions :

(A) 1. α-particles are electrically
   (i) positively charged
   (iii) neutral
                                         (ii) negatively charged
                                         (iv) none of these.
                                                        (Inter Council 1983)

2. Natural radioactivity was discovered by
   (i) Rutherford
   (iii) Madame Curie
                                         (ii) Henry Becquerel
                                         (iv) Schmidt.

3. Half-life of a radioactive substance is
   (i) dependent on initial concentration,
   (ii) independent of initial concentration.
                                                        (Inter Council 1983)

4. The half life period of a radioactive substance is 5670 years, its half-life period will change
   (i) when number of radioactive atoms are changed
   (ii) when it is subjected to pressure
   (iii) when it is heated.
   (iv) none of the above will have any effect on the half life period of the substance.
                                                        (AIIMS TEST 1981)

5. The end product of $(4n+2)$ disintegration series is
   (i) $_{82}Pb^{206}$
   (iii) $_{82}Pb^{207}$
                                         (ii) $_{82}Pb^{208}$
                                         (iv) $_{82}Bi^{202}$.

6. Number of α and β particles emitted by $_{90}Th^{232}$ in changing to a stable isotope of lead $_{82}Pb^{208}$ is
   (i) 4, 3   (ii) 5, 4   (iii) 3, 4   (iv) 6, 4.

7. In order for the chain reaction during the fission of uranium to continue, the particle that is most necessary is the

(i) alpha   (ii) proton   (iii) electron   (iv) neutron.

8. The given nuclear reaction belongs to which type of the following ?

$$_1H^2 + _1H^3 \rightarrow _2He^4 + _0n^1 + 17\cdot6 \text{ MeV.}$$

(i) Nuclear fission   (ii) Nuclear fusion
(iii) Spallation   (iv) None of these.

9. Nuclear reactions differ from ordinary reactions in all but one of the following ways :

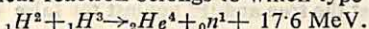(i) Nuclear reactions occur much more rapidly.
(ii) The energy evolved per gram is much greater for nuclear reactions.
(iii) New elements are often formed in nuclear reactions.
(iv) In nuclear reactions reactivity is essentially independent of the state of chemical combination.

10. In the following radioactive disintegration

$$_{94}Pu^{239} ----\rightarrow _{95}Am^{239} + x$$
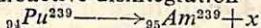
The symbol 'x' represents

(i) an electron   (ii) a proton
(iii) a neutron   (iv) an alpha particle.

11. Which one of the following is a radioactive substance ?

(i) Heavy hydrogen   (ii) Nascent hydrogen
(iii) Tritium   (iv) Atomic hydrogen.

12. The half-life period of a radioactive substance depends on

(i) initial amount of the substance (ii) disintegration constant
(iii) temperature   (iv) none of these.

13. Which of the following has the greatest penetrating power ?

(i) α-rays (ii) β-rays (iii) Gamma rays (iv) none of these.

14. α-rays are

(i) H^+ ions   (ii) He^{++} ions   (iii) He atoms   (iv) electrons.

15. The first artificial transmutation of elements was carried out by

(i) Madame Curie   (ii) Irene Curie
(iii) Rutherford   (iv) Soddy.

16. Loss of one α-particle followed by two β-particles results in the formation of

(i) isomer   (ii) isobar   (iii) isotone,   (iv) isotope.

17. Isotopes differ in

(i) the number of protons   (ii) the valency number
(iii) the chemical activity   (iv) the number of neutrons.

18. The atomic weight of carbon, nitrogen and oxygen are 12, 14 and 16 respectively. An atom of atomic weight 14 and nuclear charge of +6 is an isotope of

(i) oxygen (ii) nitrogen (iii) carbon (iv) carbon dioxide (v) ammonia.

19. The particle having negative charge and mass equal to 273 times the mass of electron having half-life of 10^{-8} second is

(i) negative Pi-meson,   (ii) neutral Pi meson,
(iii) μ-meson,   (iv) anticharged K-meson.

20. The phenomenon of emitting radiation which can affect a photographic plate is known as

(i) Phosphorescence   (ii) Luminescence
(iii) Radioactivity$_2$ (iv) Photo-electric effect

21. The product of the half-life period and the disintegration constant of a radioactive element is

(i) 2   (ii) 1   (iii) 0·693   (iv) 10.

22. The reciprocal of the disintegration constant of a radioactive element is called

(i) half-life   (ii) average-life   (iii) curie   (iv) micro-curie.

(B) Assign mark 'T' against the true and 'F' against the false statements below :

1. The half-life period of a radioactive element does not depend upon the initial amount of the element.

2. The penetrating power of y-rays is greater than those of α and β-rays.

3. When a non-radioactive substance becomes radioactive under the influence of a radioactive substance, the phenomenon is called **Artificial Radioactivity.**

4. The β-particles are actually the extra-nuclear electrons present in an atom.

Ans. (A) 1. (i), 2. (ii), 3. (ii), 4. (iv), 5. (iii), 6. (iv), 7. (iv), 8. (ii), 9. (iv), 10. (i), 11. (iii), 12. (ii), 13. (iii), 14. (ii), 15. (iii), 16. (iv), 17. (iv), 18. (iii), 19. (i), 20. (iii), 21. (iii), 22. (ii).

(B) 1. T, 2. T, 3. T, 4. F.

Numerical Problems :

1. One gram of a radioactive element decays by β-emission to 0·125 g in 200 hours.   What is its half life period ?
(Ans. 66·53 hours)

2. A piece of wood recovered in an excavation has 30% as much C-14 as ordinary wood today.   When was the piece buried ?   Take the value of half-life period for C-14 as 5760 years.
(Ans. 10010 years)

3. Calculate the number of α-particles and β-particles expelled in the uranium series in reaching Pb-206 from U-238.
(Ans. α=8, β=6)

4. One mg of radioactive iodine contained in thryoxine is injected into the blood of a patient.   How long will it take for radioactivity to fall to 50%, 25% and 10% of the initial value ? $\left(t_{\frac{1}{2}} \text{ for } I_{53}^{133}=8\cdot05 \text{ d} \right)$

(Ans. 8·05 d, 16·10 d and 26·75 d)

5. A radioactive element takes two hours to reduce to half its initial amount. Calculate the disintegration constant for it.

□ □ □

OXIDATION-REDUCTION

Oxidation

Ordinarily, oxidation means the process of direct union of a substance with oxygen.

In a limited way, oxidation is defined as the process which increases the proportion of electronegative atoms or groups in a substance or diminishes the proportion of the electropositive atoms or groups in a compound.

$$C + O_2 \rightarrow CO_2 \quad \text{(oxidation of } C\text{)}$$
$$2Na + Cl_2 \rightarrow 2NaCl \quad \text{(oxidation of } Na\text{)}$$
$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3 \quad \text{(oxidation of } FeCl_2\text{)}$$
$$CuO + H_2 \rightarrow Cu + H_2O \quad \text{(oxidation of } H_2\text{)}$$
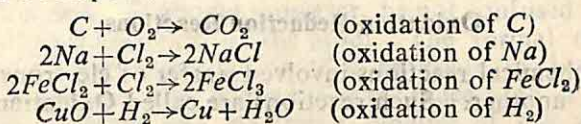
According to **ionic theory**, oxidation is defined as the process in which positive charge is increased or negative charge is decreased on an ion.

$$2Fe^{++} + Cl_2 \rightarrow 2Fe^{+++} + 2Cl^-$$
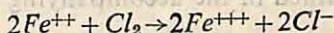
In this process, the positive charge on Fe increases from $+2$ (on Fe^{++}) to $+3$ (on Fe^{+++}). Hence, Fe^{++} is oxidised to Fe^{+++}.

Electronic concept—Oxidation is a process in which electrons are lost by an atom or group of atoms.

$$Na \rightarrow Na^+ + e$$
$$Fe^{++} \rightarrow Fe^{+++} + e$$
$$Zn \rightarrow Zn^{++} + 2e$$
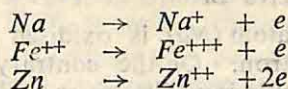
In these processes Na, Fe^{++} and Zn are oxidised to Na^+, Fe^{+++} and Zn^{++} ions respectively.

Reduction

Ordinarily, reduction means the process of direct union of a substance with hydrogen or removal of oxygen from a compound.

In a limited sense, reduction is defined as the process in which the proportion of the electropositive atoms or groups in a substance is increased or the proportion of the electronegative atoms or groups is diminished in a compound.

$$CuO + H_2 \rightarrow Cu + H_2O \text{ (reduction of } CuO\text{)}$$
$$Ca + H_2 \rightarrow CaH_2 \text{ (reduction of } Ca\text{)}$$
$$2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4 \text{ (reduction of } HgCl_2\text{)}$$
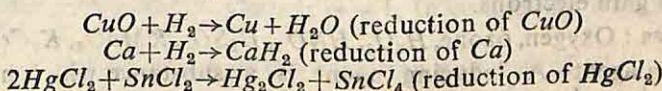
According to the ionic theory, reduction is the process in which

the positive charge is decreased or the negative charge is increased on an ion.

$$SnCl_4 \rightarrow SnCl_2$$

or

$$Sn^{4+} + 4Cl^- \rightarrow Sn^{2+} + 2Cl^-$$
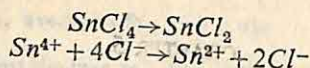
In this process, the positive charge on Sn decreases from $+4$ (on Sn^{4+}) to $+2$ (on Sn^{2+}). Hence, $SnCl_4$ is reduced to $SnCl_2$.

Electronic concept—Reduction is a process in which electrons are gained by an atom or group of atoms.

$$Cl_2 + 2e \rightarrow 2Cl^-$$
$$Fe^{+++} + e \rightarrow Fe^{++}$$
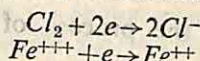
In these processes neutral Cl_2 is transformed into an anion (Cl^-), and ferric ion (Fe^{+++}) having $+3$ charge is converted to ferrous ion (Fe^{++}) having $+2$ charge.

Oxidation-Reduction Reactions

Several chemical reactions involve transfer of electrons from one reactant to another. Such reactions are called **Oxidation-reduction reactions**.

Oxidation-reduction reactions occur simultaneously. The total number of electrons lost upon oxidation is always equal to the total number of electrons gained in the accompanying reduction process.

(i) **Combination of Na and Cl :**

$$\begin{array}{ll} Na \rightarrow Na^+ + e \quad [\times 2] & \text{(oxidation)} \\ Cl_2 + 2e \rightarrow 2Cl^- & \text{(reduction)} \\ \hline 2Na + Cl_2 \rightarrow 2Na^+Cl^- & \end{array}$$
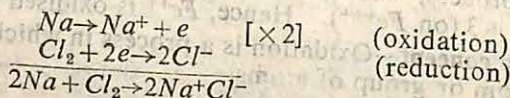
In this reaction, Sodium atom (Na) is oxidised to Sodium ion (Na^+) since it loses one electron. On the contrary, each chlorine atom (Cl) is reduced to chloride ion (Cl^-) since each Cl atom gains one electron.

(ii) **Reduction between Hg^{++} and Sn^{++} ions :**

$$\begin{array}{ll} 2Hg^{++} + 2e \rightarrow Hg_2^{++} & \text{(reduction)} \\ Sn^{++} \rightarrow Sn^{++++} + 2e & \text{(oxidation)} \\ \hline 2Hg^{++} + Sn^{++} \rightarrow Hg_2^{++} + Sn^{++++} & \end{array}$$
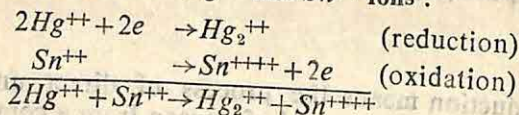
Thus, we see that both oxidation and reduction go on in a reaction together. The oxidising agent is itself reduced, whereas the reducing agent is itself oxidised.

Oxidising agent—An oxidising agent is a substance which has a tendency to gain electrons.

Examples : Oxygen, ozone, H_2O_2, HNO_3, H_2SO_4, $KMnO_4$, $K_2Cr_2O_7$.

Reducing agent—A reducing agent is a substance which has a tendency to lose electrons.

Examples : Hydrogen, H_2S, CO, SO_2, C, $FeSO_4$, $H_2C_2O_4$ (oxalic acid), $SnCl_2$ etc.

Oxidation-reduction reactions of covalent compounds

In the formation of covalent compounds there is no loss or gain of electrons. Hence, the oxidation-reduction reactions involving covalent bond formation cannot be explained on the basis of electron loss or gain. In such cases, the concept of **oxidation number** is provoked.

Oxidation number—Oxidation number is an integer which is assigned to each atom in a molecule, a complex ion or the free state in order to determine the number of electrons lost or gained in a chemical change.

Oxidation number represents the oxidation state of the atom in a molecule or ion. It should, however, be not confused with the formal charges that may exist on the atom. The formal charge is based on the real charge distribution of a molecule or ion among the constituent atoms. This is done in accordance with a detailed knowledge of structure and electronic binding of the molecule. Oxidation state is, however, independent of the type of bonding in which the atoms is concerned. However, the oxidation number does not necessarily describe the electronic state of an atom in a molecule.

Oxidation state is computed directly from the molecular formula itself.

The assignment of oxidation number follows the following rules :

(i) A positive oxidation number is assigned to the less electronegative element in a covalent compound, and a negative oxidation number is assigned to the more electronegative element.

In H_2O, H atom is assigned a +ve oxidation number, whereas O is assigned a negative oxidation number.

(ii) **The oxidation number of a free and uncombined element is zero.** This represents the fact that a free element has neither lost nor gained electrons.

Examples : H in H_2, P in P_4, O in O_2, S in S_8 etc.

In H_2, of the two electrons in the molecule, one is assigned to each H-atom. A hydrogen atom with one electron is virtually the same as a neutral free H atom. Thus, the O.N. is zero.

(iii) The oxidation number of hydrogen in its compounds is usually +1, except in the case of metallic hydrides, where it is −1.

(iv) The oxidation number of oxygen in compounds is usually −2, except in peroxides, where it is −1. In compounds with fluorine, it is positive.

(v) The algebraic sum of the oxidation numbers of all the atoms in a molecule of the compound is zero.

(vi) The algebraic sum of the oxidation numbers of all the atoms in an ion is equal to the charge of the ion.

Application of rules

(i) Oxidation number of C in CH_2O :

Let the O.N. of C be x.

The sum of the oxidation numbers of two H atoms $= +2$. Thus,

$$\overset{x}{C} \overset{+2}{H_2} \overset{-2}{O}$$
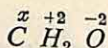
$$\therefore \quad x + 2 - 2 = 0; \qquad \text{or} \qquad x = 0.$$

(ii) Oxidation number of Fe in Fe_3O_4 :

Let the O.N. of Fe be x. Then,

$$\overset{3x}{Fe_3} \overset{-8}{O_4}$$

$$\therefore \quad 3x - 8 = 0; \qquad \text{or} \qquad x = 8/3.$$

(iii) Oxidation number of C in C_4H_6 :

Let the O.N. of C be x. Then,

$$\overset{4x}{C_4} \overset{+6}{H_6}$$

$$\therefore \quad 4x + 6 = 0; \qquad \text{or} \qquad x = -\frac{3}{2}.$$

(iv) O.N. of S in $Na_2S_4O_6$:

Let the O.N. of S be x. Then,

$$\overset{+2}{Na_2} \overset{4x}{S_4} \overset{-12}{O_6}$$
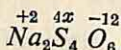
$$\therefore \quad +2 + 4x - 12 = 0$$

$$\text{or} \qquad 4x = 10; \qquad \text{or} \qquad x = \frac{5}{2}.$$

(v) O.N. of S in SO_2 :

Let the O.N. of S be x. Then,

$$\overset{x}{S} \overset{-4}{O_2}$$

$$\therefore \quad x - 4 = 0; \qquad \text{or} \qquad x = +4.$$

(vi) O.N. of Mn in $KMnO_4$:

Let the O.N. of Mn be x. Then,

$$\overset{+1}{K} \overset{x}{Mn} \overset{-8}{O_4}$$
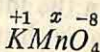
$$\therefore \quad +1 + x - 8 = 0; \qquad \text{or} \qquad x = +7.$$

(vii) O.N. of Cr in $K_2Cr_2O_7$:

Let the O.N. of Cr be x. Then,

$$\overset{+2}{K_2} \overset{2x}{Cr_2} \overset{-14}{O_7}$$
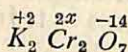
$$\therefore \quad +2 + 2x - 14 = 0$$

$$\text{or} \qquad 2x = +12; \qquad \text{or} \qquad x = +6.$$

(viii) O.N. of S in SO_4^{2-} :

Let the O.N. of S be x. Then,

$$\left(\overset{x}{S}\,\overset{-8}{O_4}\right)^{2-}$$
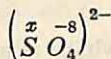
$\therefore$ $x - 8 = -2$;   or $x = +8 - 2 = +6$.

(ix) O.N. of P in PH_3 :

P is more electronegative than H. Hence, it would be assigned a negative O.N. Let it be x. Then,

$$\overset{x}{P}\,\overset{+3}{H_3}$$

$\therefore$ $x + 3 = 0$;   or $x = -3$.

(x) O.N. of F in F_2O :

As F is more electronegative than O, it would be assigned a negative O.N. Let it be x. Then,

$$\overset{2x}{F_2}\,\overset{+2}{O}$$

$\therefore$ $2x + 2 = 0$;   or $x = -1$.

(xi) Oxidation number of S in (a) $H_2S_2O_6$ and (b) $H_2S_2O_8$:

(a) $H_2S_2O_6$:

Let the O. N. of S in $H_2S_2O_6$ be x. Then,

$$\overset{+2}{H_2}\,\overset{2x}{S_2}\,\overset{-12}{O_6}$$
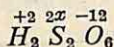
$\therefore$ $+2 + 2x - 12 = 0$

or $2x = 10$;   or $x = +5$.

(b) Let the O. N. of S in $H_2S_2O_8$ be x. Then,

$$\overset{+2}{H_2}\quad\overset{2x}{S_2}\quad\overset{-16}{O_8}$$
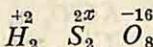
$\therefore$ $+2 + 2x - 16 = 0$

or, $2x = 14$;   or $x = +7$.

But the maximum valency of S is only 6 and in no case the O. N. of S can exceed the maximum valency. Hence, we will have to consider the structure of $H_2S_2O_8$.

$$\begin{array}{c} \quad\quad\overset{\displaystyle O}{\|}\quad\quad\quad\quad\overset{\displaystyle O}{\|} \\ H-O-S-O-O-S-O-H \\ \quad\quad\underset{\displaystyle O}{\|}\quad\quad\quad\quad\underset{\displaystyle O}{\|} \end{array}$$
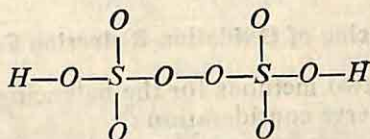
We see that there is a $O-O$ bond in the structure involving two O atoms. Hence, of the eight O atoms two will have O. N. -1, and the remaining six will have O. N. -2.

Now $2(+1) + 2(x) + 6(-2) + 2(-1) = 0$

or $2 + 2x - 12 - 2 = 0$

or $2x = 12$;   or $x = +6$.

Oxidation and Reduction on the basis of O. N.

The definitions of oxidation and reduction may now be given as :

Oxidation : The process which is accompanied with the increase in oxidation number is called oxidation.

Reduction : The process which is accompanied with decrease in oxidation number is called reduction.

Example : (i)

$$\overset{0}{2Na} + \overset{0}{Cl_2} \longrightarrow \overset{+1\ -1}{2NaCl}$$

O.N. increases

O.N. dicreases
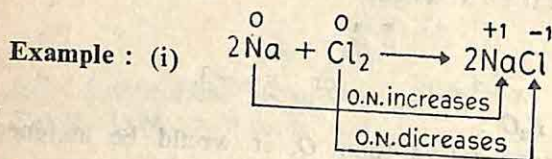
In this reaction, oxidation number of Na increases from 0 to $+1$. Hence, Na is oxidised. Na, therefore, acts as a reducing agent. On the other hand, oxidation number of Cl_2 decreases from 0 to -1. Hence, Cl_2 is reduced. Cl_2 is, therefore, an oxidising agent.

(ii)

$$\overset{+5}{KClO_3} + 3\overset{+2}{Na_2SnO_2} \longrightarrow \overset{-1}{KCl} + 3\overset{+4}{Na_2SnO_3}$$

O.N. decreases
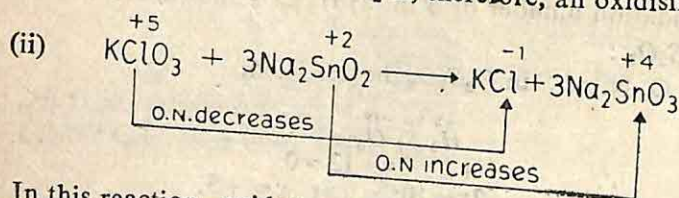
O.N increases

In this reaction, oxidation number of chlorine decreases from $+5$ to -1 ($KClO_3 \rightarrow KCl$), whereas that of Sn increases from $+2$ to $+4$ ($Na_2SnO_2 \rightarrow Na_2SnO_3$). $KClO_3$ is, therefore, reduced, whereas Na_2SnO_2 is oxidised. Hence, $KClO_3$ acts as an oxidising agent, and Na_2SnO_2 acts as a reducing agent.

Oxidising agent : A substance that causes an increase in the oxidation number of another substance is called an oxidising agent.

Reducing agent : A substance that causes a decrease in the oxidation number of another substance is called a reducing agent.

Balancing of Oxidation-Reduction Equations

The following two methods for the balancing of oxidation-reduction equations deserve consideration :

A. Ion-electron method : This method is based on the fact that the total number of electrons lost by one substance on oxidation is always equal to the total number of electrons gained by another substance in the accompanying reduction process.

The steps followed in this method are :

(i) A skeleton equation including the reactants and the products is written.

(ii) A partial skeleton equation is written for the oxidising agent.

(iii) A partial skeleton equation is written for the reducing agent.

(iv) Each partial equation is now balanced as to the number of atoms of each element.

(v) Each partial equation is then balanced as to the number of charges by adding an appropriate number of electrons either to the left or to the right side of the equation.

(vi) Each partial equation is multiplied by a suitable number such that the total number of electrons lost by the reducing agent is equal to the total number of electrons gained by the oxidising agent.

(vii) Finally, the two partial equations are added together to get the over-all balanced oxidation-reduction equation, any term common to both sides being cancelled.

Examples : 1. Oxidation of Copper by Nitric acid :

$$Cu + H^+ + NO_3^- \rightarrow Cu^{++} + NO + H_2O$$
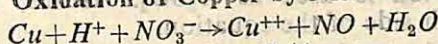
Step I. Oxidation : $Cu \rightarrow Cu^{++}$
Reduction : $NO_3^- \rightarrow NO$

Step II. Oxidation half equation is already balanced with respect to Cu atom. Reduction half reaction is balanced by adding $4H^+$ to the left and $2H_2O$ to the right.

Oxidation : $Cu \rightarrow Cu^{++}$
Reduction : $NO_3^- + 4H^+ \rightarrow NO + 2H_2O$

Step III. Charges on both sides are balanced by adding electrons.

Oxidation : $Cu \rightarrow Cu^{++} + 2e$
Reduction : $NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O$

Step IV. Oxidation half reaction is multiplied by 3 and reduction half reaction by 2 to cancel the electrons when both the half reactions are added.

Oxidation : $[Cu \rightarrow Cu^{++} + 2e] \times 3$
Reduction : $[NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O] \times 2$

$$\overline{3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{++} + 2NO + 4H_2O}$$
$$3Cu^{++} + 6NO_3^- \rightarrow 3Cu(NO_3)_2$$

$$\overline{3Cu + 8NO_3^- + 8H^+ \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O}$$
or $\quad 3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

2. Oxidation of Cl^- by MnO_4^- :

$$KMnO_4 + KCl + H_2SO_4 \rightarrow MnSO_4 + K_2SO_4 + H_2O + Cl_2$$
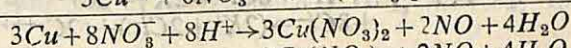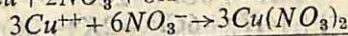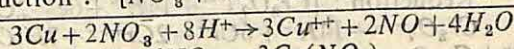
Step I. Oxidation : $Cl^- \rightarrow Cl_2$
Reduction : $MnO_4^- \rightarrow Mn^{++}$

Step II. Both oxidation and reduction equations are balanced with respect to atoms.

Oxidation : $2Cl^- \rightarrow Cl_2$
Reduction : $MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$

Step III. Charges are balanced.

Oxidation : $\qquad 2Cl^- \rightarrow Cl_2 + 2e$

Reduction : $\qquad MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$

Step IV. Oxidation half equation is multiplied by 5 and reduction half equation by 2 to get a balanced number of electrons.

Oxidation : $\qquad [2Cl^- \rightarrow Cl_2 + 2e] \times 5$

Reduction : $[MnO_4^- + 8H + 5e \rightarrow Mn^{++} + 4H_2O] \times 2$
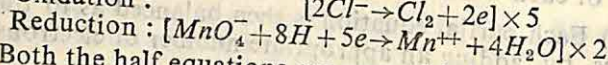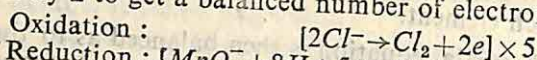
Step V. Both the half equations are now added up.

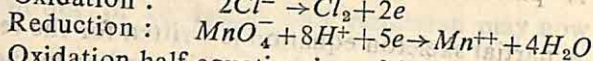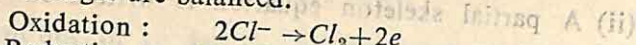$$2MnO_4^- + 10Cl^- + 16H^+ \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2$$
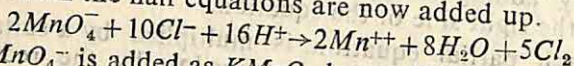
Since MnO_4^- is added as $KMnO_4$ hence $2MnO_4^-$ bring with it $2K^+$ ions to the left. K^+ ion, however, does not participate in the reaction and it appears as such on the right side also.

Cl^- ion was used as KCl. Hence $10Cl^-$ ions will introduce $10K^+$ ions to the left and they appear unreacted on the right side also.

Thus, $12K^+$ ions are added on both sides of the above equation.

Now, H^+ ion is used as H_2SO_4. Hence, $16H^+$ ions bring in $8SO_4^{--}$ to each side of the equation.
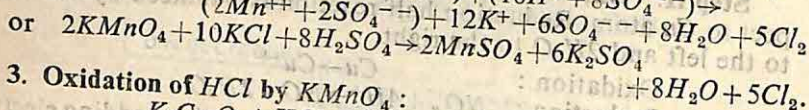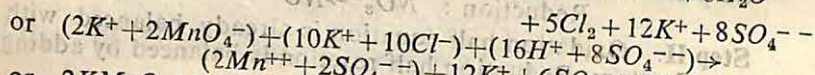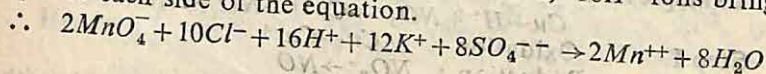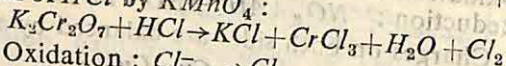
$$\therefore \quad 2MnO_4^- + 10Cl^- + 16H^+ + 12K^+ + 8SO_4^{--} \rightarrow 2Mn^{++} + 8H_2O$$
$$+ 5Cl_2 + 12K^+ + 8SO_4^{--}$$

or $(2K^+ + 2MnO_4^-) + (10K^+ + 10Cl^-) + (16H^+ + 8SO_4^{--}) \rightarrow$
$$(2Mn^{++} + 2SO_4^{--}) + 12K^+ + 6SO_4^{--} + 8H_2O + 5Cl_2$$

or $2KMnO_4 + 10KCl + 8H_2SO_4 \rightarrow 2MnSO_4 + 6K_2SO_4$
$$+ 8H_2O + 5Cl_2.$$

3. Oxidation of HCl by $KMnO_4$:

$$K_2Cr_2O_7 + HCl \rightarrow KCl + CrCl_3 + H_2O + Cl_2$$

Step I. Oxidation : $Cl^- \rightarrow Cl_2$

Reduction : $Cr_2O_7^{--} \rightarrow Cr^{+++}$

Step II. Oxidation : $2Cl^- \rightarrow Cl_2$

Reduction : $Cr_2O_7^{--} + 14H^+ \rightarrow 2Cr^{+++} + 7H_2O$

Step III. Oxidation : $2Cl^- \rightarrow Cl_2 + 2e$

Reduction : $Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O$
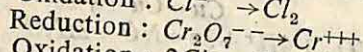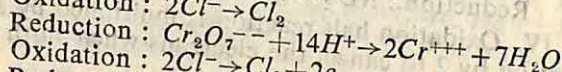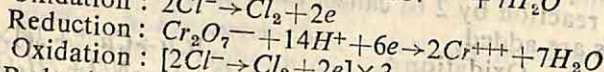
Step. IV. Oxidation : $[2Cl^- \rightarrow Cl_2 + 2e] \times 3$

Reduction : $[Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+++} + 7H_2O] \times 1$

Step V. $Cr_2O_7^{--} + 14H^+ + 6Cl^- \rightarrow 2Cr^{+++} + 7H_2O + 3Cl_2$

or, $(2K^+ + Cr_2O_7^{--}) + 14H^+ + 6Cl^- \rightarrow 2K^+ + 2Cr^{+++} + 7H_2O + 3Cl_2$
$$+ 8Cl^- \rightarrow (2K^+ + 2Cl^-) + (2Cr^{+++} + 6Cl^-)$$
$$+ 7H_2O + 3Cl_2$$

or, $K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$
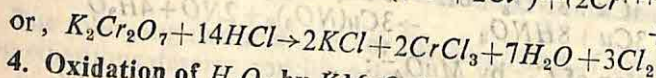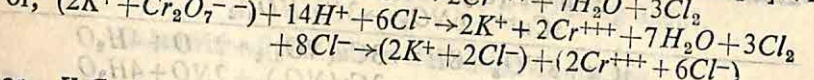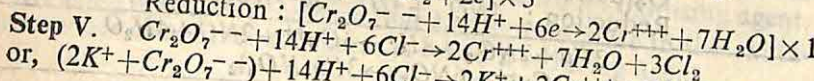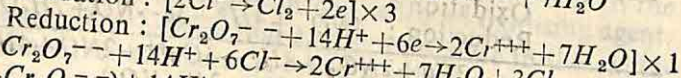
4. Oxidation of H_2O_2 by $KMnO_4$ in presence of H_2SO_4 :

$$KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow MnSO_4 + K_2SO_4 + O_2 + H_2O$$
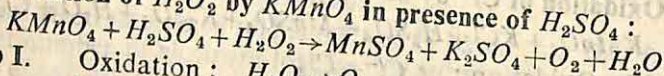
Step I. Oxidation : $H_2O_2 \rightarrow O_2$

Reduction : $MnO_4^- \rightarrow Mn^{++}$

Step II. Oxidation : $H_2O_2 \rightarrow O_2 + 2H^+$

Reduction : $MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O$
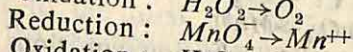
Step III. Oxidation : $H_2O_2 \rightarrow O_2 + 2H^+ + 2e$
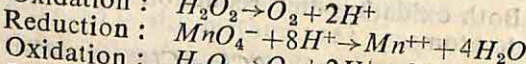
Reduction : $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$
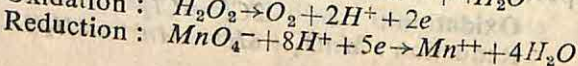
Step IV. Oxidation : $[H_2O_2 \rightarrow O_2 + 2H^+ + 2e] \times 5$

Reduction : $[MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O] \times 2$

Step V. $2MnO_4^- + 16H^+ + 5H_2O_2 \rightarrow 2Mn^{++} + 8H_2O + 5O_2 + 10H^+$

or $\qquad 2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{++} + 8H_2O + 5O_2$

or $\qquad (2K^+ + 2MnO_4^-) + (6H^+ + 3SO_4^{--}) + 5H_2O_2 \rightarrow$

$\qquad\qquad (2Mn^{++} + 2SO_4^{--}) + (2K^+ + SO_4^{--}) + 8H_2O + 5O_2$

or $\quad 2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2$

B. Oxidation Number Method :

In order to balance an oxidation-reduction equation by Oxidation number method the following steps are usually adopted :

(i) A skeleton equation is first written including all the reactants and the products.

(ii) Oxidation number for all the elements in each formula is indicated.

(iii) The elements whose oxidation numbers change in the reaction are identified.

(iv) Electron gains or losses are shown for those elements whose oxidation numbers change.

(v) The number of electrons gained or lost are equated.

(vi) The residual part of the equation is finally balanced by inspection and applying our intuition.

Examples : 1. Oxidation of H_2S by HNO_3 :

$$HNO_3 + H_2S \rightarrow NO + S + H_2O$$
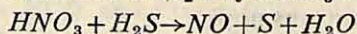
In this reaction, the oxidation number of N decreases from $+5$ (in NO_3^- ion) to $+2$ (in NO), and the oxidation number of S increases from -2 (in H_2S) to 0 (in S).

$$\text{(i)} \quad N^{+5} + 3e \rightarrow N^{+2}$$
$$\text{(ii)} \quad S^{-2} \rightarrow S^0 + 2e$$

The electrons in these equations are now balanced.

$$[N^{+5} + 3e \rightarrow N^{+2}] \qquad \times 2$$
$$[S^{-2} \qquad \rightarrow S^0 - 2e] \quad \times 3$$

Hence, the co-efficient of HNO_3 and NO is 2, whereas that of H_2S and S is 3.

$\therefore \qquad\qquad 2HNO_3 + 3H_2S \rightarrow 2NO + 3S + H_2O$

The 8 H atoms on the left are capable of forming $4H_2O$.

$\therefore \qquad\qquad 2HNO_3 + 3H_2S \rightarrow 2NO + 3S + 4H_2O.$

2. Reduction of Fe^{++} by $Cr_2O_7^{--}$ in acid medium :
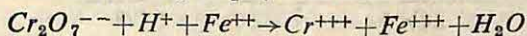
$$Cr_2O_7^{--} + H^+ + Fe^{++} \rightarrow Cr^{+++} + Fe^{+++} + H_2O$$
$$Cr_2O_7^{--} \rightarrow 2Cr^{+++}$$
$$Fe^{++} \rightarrow Fe^{+++}$$

In this reaction, the O. N. of Cr decreases from $+6$ (in $Cr_2O_7^{--}$) to $+3$ (in Cr^{+++}), and the O. N. of Fe increases from $+2$ (in Fe^{++})

to $+3$ (in Fe^{+++}).

$\therefore$ Change in O. N. of $Cr = 2\times6 - 2\times3 = 6$

     Change in O. N. of $Fe = 3 - 2 = 1$

$\therefore$ $Cr_2O_7^{--} + 6e \to 2Cr^{+++}$

                          $Fe^{++} \to Fe^{+++} + e$
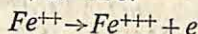
Acid provides H^+ ions to the solution which convert all the O atoms to H_2O.

i.e., $Cr_2O_7^{--} + 14H^+ + 6e \to 2Cr^{+++} + 7H_2O$

                  $[Fe^{++} \qquad \to Fe^{+++} + e] \quad \times 6$

Adding : $\overline{Cr_2O_7^{--} + 14H^+ + 6Fe^{++} \to 2Cr^{+++} + 6Fe^{+++} + 7H_2O}$
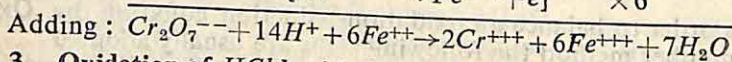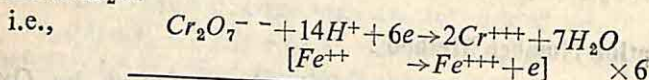
3. **Oxidation of HCl by MnO_4^- :**

$$MnO_4^- + HCl \to MnCl_2 + Cl_2 + H_2O$$
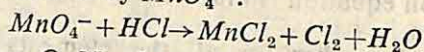
In this reaction, O. N. of Mn decreases from $+4$ (in MnO_4^-) to $+2$ (in $MnCl_2$), and the O. N. of Cl increases from -1 (in HCl) to 0 (in Cl_2).

$$Mn^{+4} \to Mn^{+2}$$
$$Cl^{-1} \to Cl^0$$
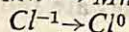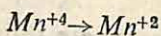
$\therefore$ Change in O. N. of $Mn = 7 - 2 = 5$

     Change in O. N. of $Cl = 1$

$\therefore$ $Mn^{+7} + 5e \to Mn^{+2}$

                          $Cl^{-1} \to Cl^0 + e$
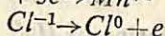
Balancing of electrons now,

              $[Mn^{+7} + 5e \to Mn^{+2} \qquad \times 2$

              $[Cl^{-1} \to Cl^0 + e] \qquad \times 10$
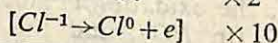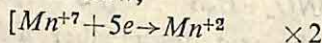
Thus, for co-efficient, for MnO_4^- and $MnCl_2$ is that for HCl and Cl is 10.

$\therefore$ $2MnO_4^- + 10HCl \to 2MnCl_2 + 8H_2O + 5Cl_2$

or $(2K^+ + 2MnO_4^-) + 16 HCl \to 2MnCl_2 + 2KCl + 8H_2O + 5Cl_2$

or $2KMnO_4 + 16HCl \to 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$.
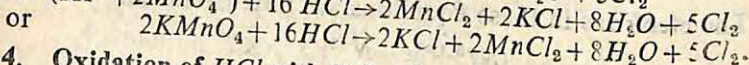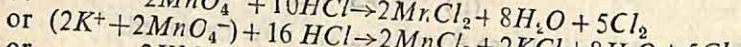
4. **Oxidation of HCl with $K_2Cr_2O_7$ in acidic medium :**

           $K_2Cr_2O_7 + HCl \to KCl + CrCl_3 + H_2O + Cl_2$

Oxidation : $2Cl^{-1} \to 2Cl^0$

or $2Cl^{-1} \to 2Cl^0 + 2e$

Reduction : $2Cr^{+6} \to 2Cr^{+3}$

or $2Cr^{+6} + 6e \to 2Cr^{+3}$

Multiplying : $[2Cl^{-1} \to 2Cl^0 + 2e] \times 3$

                          $[2Cr^{+6} + 6e \to 2Cr^{+3}] \quad \times 1$

Adding : $\overline{2Cr^{+6} + 6Cl^{-1} \to 2Cr^{+3} + 6Cl^0}$

$\therefore$ $K_2Cr_2O_7 + 6HCl \to 2CrCl_3 + 3Cl_2$ (Incomplete)
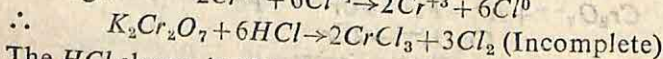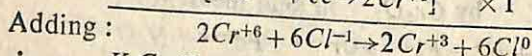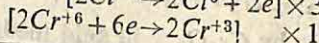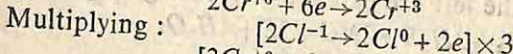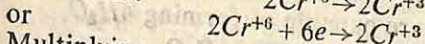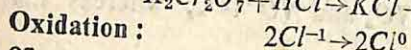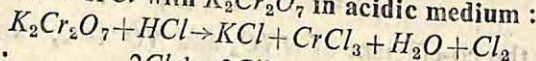
The HCl shown in this equation acts as a reducing agent. Now, we have to introduce KCl, H_2O and HCl (which acts as an acid) in this equation.

We see that 7 atoms of Oxygen in $K_2Cr_2O_7$ form $7\,H_2O$. For this we need 14 H atoms which would be provided by 14 HCl. As six of the Cl^- ions are oxidised to Cl_2, the remaining $(14-6=8)$ should appear on the right as KCl or $CrCl_3$. Again, 1 $K_2Cr_2O_7$ gives 2 KCl. Hence,

$$K_2Cr_2O_7 + 14HCl \rightarrow 2CrCl_3 + 2KCl + 7H_2O + Cl_2.$$

Comparison between the Ion-electron Method and the Oxidation number Method :

The ion-electron method appears to be more appropriate on the following grounds :

(i) It draws a distinction between the components which react and that which do not react.

(ii) The half reactions of the partial equations can actually be made to take place independently.

Disproportionation reactions :

There are some substances which behave as oxidising as well as reducing agent under the same set of conditions, i.e. the same substance undergoes oxidation and reduction both. Such a reaction is called a **disproportionation reaction.**

Examples : (i) $3K\overset{+1}{Cl}O \rightarrow 2KCl^{-1} + K\overset{+5}{Cl}O_3$

Potassium hypochlorite decomposes to give Potassium chloride and Potassium chlorate. The O. N. of Cl decreases from $+1$ (in $KClO$) to -1 (in KCl) and increases to $+5$ (in $KClO_3$). $KClO$ is thus reduced in the change, $KClO \rightarrow KCl$, but is oxidised in its change $KClO \rightarrow KClO_3$. Thus, $KClO$ acts both as an oxidant and a reductant.

(ii)

$$2\overset{+1}{Cu^+} \longrightarrow Cu^\circ + \overset{+2}{Cu^{++}}$$

Reduction
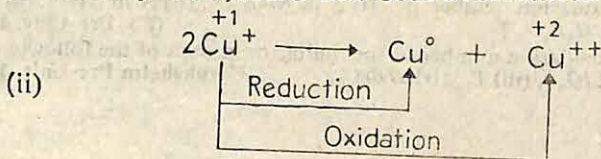
Oxidation

Cu^+ ion thus acts as an oxidant and a reductant at the same time.

(iii)

$$\overset{\circ}{Cl_2} + H_2O \longrightarrow \overset{-1}{H}Cl + \overset{+1}{H}ClO$$

Reduction
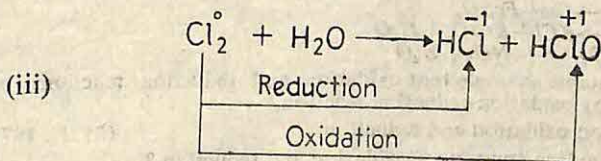
Oxidation

Cl_2 is thus oxidised as well as reduced in this reaction.

Questions

Long Answer Type :

1. Define the terms Oxidation and Reduction in the light of the electronic concept.

2. Tell why a reducing agent itself becomes oxidised when it causes another substance to undergo reduction.

3. Balance the following equations by ion-electron method :

(i) $Fe^{++} + Cr_2O_7 -- + H^+ \rightarrow Fe^{+++} + Cr^{+++} + H_2O$
(ii) $ClO_3 - + CrO_2 - + OH - \rightarrow ClO - + CrO_4 -- + H_2O$
(iii) $HI + H_2SO_4 \rightarrow H_2O + H_2S + I_2$
(iv) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + N_2 + H_2O$

4. Balance the following equations by oxidation number method :

(i) $K_2MnO_4 + H_2O \rightarrow MnO_2 + KMnO_4 + KOH$
(ii) $Cr_2O_7 -- + H^+ + Fe^{++} \rightarrow Cr^{+++} + Fe^{+++} + H_2O$
(iii) $P + OH - \rightarrow PH_3 + H_2PO_2 -$

5. Explain Oxidation-reduction reactions. Prove that both these reactions occur simultaneously.   (Mithila U. 1974 A)

6. Indicate, with reasons, whether the underlined substances are oxidised or reduced in each of the following reactions.

(i) $\underline{Zn}$ (s) $+ 2H^+$(aq)$\rightarrow Zn^{++}$(aq)$+ H_2$(g)

(ii) Cl_2(aq)$+ SO_3 --$(aq)$+ H_2O(l) \rightarrow 2Cl^-(aq)+ SO_4 --(aq)+ 2H^+$(aq)

(iii) $2I^-$(aq)$+ Cl_2$(aq)$\rightarrow 2Cl^-$(aq)$+ I_2$(s).   (I. S. C. Delhi 1977)

7. In each of the following unbalanced equations, identify (a) the oxidation-reduction reactions, (b) the oxidising agent, (c) the reducing agent, (d) the substance oxidised, (e) the substance reduced :

(i) $Fe + Cl_2 \rightarrow FeCl_2$
(ii) $K_2Cr_2O_7 + HCl \rightarrow KCl + CrCl_3 + H_2O + Cl_2$
(iii) $NaCl + HnO_2 + H_2SO_4 \rightarrow NaHSO_4 + MnSO_4 + H_2O + Cl_2$
(iv) $Al + CuSO_4 \rightarrow Al_2(SO_4)_3 + Cu.$

8. (a) Give the oxidation number of (i) S in H_2SO_4, (ii) S in $Na_2S_2O_3$ (iii) Mn in $KMnO_4$, (iv) Cr in $K_2Cr_2O_7$, (v) C in $CHCl_3$ and (vi) N in $NaNO_3$.
                                                                 (Bombay F. Yr. 1972)

9. What is the oxidation number of (i) S in $Na_2S_2O_3$, (ii) N in $NO_2 -$, (iii) Mn in $KMnO_4$, (iv) P in $H_2P_2O_7$?   (Pb. Pre Univ. 1972)

10. What is the oxidation number of the halogens in each of the following ?
(i) HIO_3, (ii) $ClO_3 -$, (iii) F_2, (iv) $HBrO_2$.   (Kurukshetra Pre-Univ. 1972)

Short Answer Type :

1. In each of the following reactions, indicate (a) the oxidation number of each element, (b) the oxidising agent, (c) the reducing agent, and (d) the change in oxidation number that occurs for each oxidation-reduction pair :

(i) $CuSO_4 + Fe \rightarrow Cu + FeSO_4$
(ii) $KOH + Cl_2 \rightarrow KCl + KClO_3 + H_2O$
(iii) $H_2S + HNO_3 \rightarrow S + .NO_2 + H_2O$

2. Show by a suitable example that oxidation and reduction reactions occur simultaneously in any oxidation-reduction reaction.

3. Write a note on oxidation and reduction.   (M. U. 1977 A)

4. What is the modern concept of oxidation and reduction ?
                                                                 (I. S. C. Delhi 1977)

5. What is oxidation number ?   (B. U. 1978)

6. Indicate, showing reasons, which substance is oxidant and which is reductant in the following equation ?
$Cu^{2+} + 2I^{-1} \rightarrow CuI + \frac{1}{2}I_2$ (I. S. C. Delhi 1978)
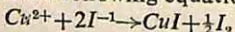
7. Show, giving reasons, which element in the following equation is oxidised :
$Mg + 2H^+ \rightarrow Mg^{++} + H_2$ (I. S. C. Delhi 1980)

8. Explain which of the following reactions is oxidation and which one is reduction :

(i) $Cu^{++} + 2e \rightarrow Cu$
(ii) $S^{--} \rightarrow S + 2e$
(iii) $S + 2e \rightarrow S^{--}$
(iv) $Zn \rightarrow Zn^{++} + 2e$.

9. Find out the oxidation number of all the atoms in the following :

(i) SO_3^{2-}, (ii) BaO_2, (iii) LiH, (iv) $C_2O_4^{2-}$, (v) N_2H_4. **(I. I. T. 1978)**

10. Find out the oxidised substance and the reduced substance in the following reactions :

(i) $2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$
(ii) $2KOH + Br_2 \rightarrow KBr + KBrO + H_2O$
(iii) $Mg + 2HCl \rightarrow MgCl_2 + H_2$. **(I. I. T. 1977)**

11. Calculate the O.N. of Nitrogen in the following :
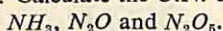
NH_3, N_2O and N_2O_5. **(B. U. 1978)**

12. Give the oxidation number of the underlined element in the following formulas :

(i) $\underline{S}^{--}$, (ii) $\underline{S}_8$, (iii) $\underline{P}O^3_{-4}$, (iv) $KM\underline{n}O_4$, (v) $(\underline{N}H_4)^+$, (vi) $(O\underline{H})^-$, (vii) $Ca(C\underline{r}O_4$

(viii) $KC\underline{l}O_4$, (ix) $(Fe\underline{C}N_6)^{4+}$.

13. Determine the O.N. of atoms which are underlined in the following compounds :
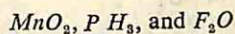
$$\underline{Mn}O_2, \underline{P}H_3, \text{ and } \underline{F}_2O$$ **(Bihar Engg. Test 1979)**

14. What do you mean by disproportionation reaction ? Explain with example. **(B. U. 1975)**

15. Which of the following equations represent oxidation-reduction reaction ?

(a) $Zn + S \rightarrow ZnS$
(b) $H^+ + OH^- \rightarrow H_2O$
(c) $MnO_2 + 2Cl^- + 4H^+ \rightarrow Mn^{++} + Cl_2 + 2H_2O$
(d) $CaO + H_2O \rightarrow Ca^{++} + 2OH^-$

Objective Questions :

Select the correct answer :

(A) 1. Oxidation is defined as

(i) gain of protons (ii) decrease in +ve valency (iii) loss of electrons (iv) in crease in −ve valency.

2. Reduction is defined as

(i) increase in +ve Valency (ii) gain of electrons (iii) loss of protons decrease in −Ve valency.

3. An oxidising agent is a substance which can

(i) accept electrons (ii) donate electrons (iii) accept protons (iv) donate (iv) protons.

4. Which one of the following can behave as an oxidising agent as well as a reducing agent ?

(i) $KMnO_4$ (ii) $K_2Cr_2O_7$ (iii) H_2S (iv) H_2O_2.

5. Which one of the following hydrides is the most powerful reducing agent ?

(i) LiH (ii) CH_4 (iii) NH_3 (iv) HF.

6. The oxidation number of nitrogen in micro-cosmic salt, $[Na(NH_4)HPO]$ is

(i) 2 (ii) 3 (iii) 5 (iv) 7.

7. When $SnCl_4$ changes to $SnCl_2$, it is said to be reduced, because :

(i) Sn is electropositive
(ii) its positive valency decreases

(iii) it loses electrons
(iv) it is electronegative.

8. A metal ion M^{+2} after losing two electrons in a reaction has an oxidation number of
(i) $+2$ (ii) $+4$ (iii) -2 (iv) 0.

9. A reducing agent is a substance which can (i) accept electrons (ii) donate electrons (iii) accept protons (iv) donate protons.

10. The O.S. of C in CH_2F_2 is
(i) $+4$ (ii) -4 (iii) 0   (iv) -1 (v) $+3$.

11. In which of the following the O.S. of N is -1 ?
(i) NH_3 (ii) NH_3NH_2 (iii) NH_2OH (iv) N_2O.

12. The O.S. of Ag in $[Ag(NH_3)_2]Cl$ is
(i) $+1$ (ii) $+2$ (iii) $+3$ (iv) $+4$.

13. The O.S. of C in $Ca(HCO_3)_2$ is (i) $+1$, (ii) $+2$, (iii) $+3$, (iv) $+4$.

14. In which of the following the O.S. of Cl is $+7$?
(i) ClO^- (ii) ClO_2 (iii) ClO_3 (iv) ClO_4^-.

15. The oxidation state of underlined element in $K_4[\underline{Fe}(CN)_2$ is,
(i) $+2$ (ii) $+3$ (iii) $+4$ (iv) $+5$.

16. Addition of iron scraps to $CuSO_4$ solution precipitates copper due to
(i) reduction of Cu^{++}, (ii) reduction of SO_4^{--},
(iii) reduction of Fe, (iv) hydrolysis of $CuSO_4$.

17. Indicate which of the following reactions is an oxidation one :
(i) $Mn \rightarrow Mn^{++} + 2e$
(ii) $NaOH + HCl \rightarrow NaCl + H_2O$
(iii) $Fe^{+++} + e \rightarrow Fe^{++}$
(iv) $Sn^{+4} + 2e \rightarrow Sn^{+2}$.

18. The most common oxidation state of an element is -2. The number of electrons present in the outermost shell of its atom is
(i) 4   (ii) 2   (iii) 6   (iv) 8.

19. The equivalent weight of $KMnO_4$ in acid medium is
(i) M,   (ii) M 2   (iii) $M/3$,   (iv) $M/4$,   (v) $M/5$.

20. The equivalent weight of $K_2Cr_2O_7$ in acid medium is
(i) M (ii) $M/3$ (iii) $M/5$ (iv) $M/6$.

21. When NH_4OH is added to $CuSO_4$ solution a deep blue coloured solution of $[Cu(NH_3)_4]SO_4$ is obtained. In this reaction copper ion is
(i) Oxidised
(ii) reduced
(iii) both oxidised and reduced
(iv) none of the above.

22. In the reaction, $2Cu^+ \rightarrow Cu + Cu^{++}$, Cu^+ ion is
(i) oxidised.
(ii) reduced
(iii) both oxidised and reduced
(iv) none of the above

23. In the reaction, $2H_2S + SO_2 \rightarrow 2H_2O + 3S$, the substance that is oxidised is
(i) H_2S (ii) SO_2
(iii) H_2S and SO_2 both,   (iv) none of these.

24. The oxidation state of oxygen in H_2O_2 is
(i) -2 (ii) -1 (iii) 0   (iv) $+1$.

25. In the reaction, $2CuSO_4 + 4KI \rightarrow Cu_2I_2 + I_2 + K_2SO_4$ the equivalent weight of Cu is
(i) 63·5   (ii) 31·8   (iii) 6·35   (iv) 137·0   (v) 13·7.

26. Zinc reacts with dil. H_2SO_4 according to the following equation :
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
In this reaction, Zinc is said to be
   (i)   oxidised
   (ii) reduced
   (iii) neither oxidised nor reduced
   (iv) both oxidised and reduced.
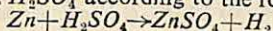
27. In the reaction, $PbO_2 + 4HCl \rightarrow PbCl_2 + H_2O$,
   (i) Pb is oxidised
   (ii) Pb is reduced
   (iii) Pb is neutralised
   (iv) no change occurs.

28. In the reaction, $Na_2SO_3 + H_2O_2 \rightarrow Na_2SO_4 + H_2O$
   (i)   hydrogen peroxide acts as a reducing agent
   (ii) sodium sulphite oxidises hydrogen peroxide to water
   (iii) sodium sulphite is oxidised.

29. A reducing agent is a substance that
   (i)   may give hydrogen to another substance
   (ii) may increase the proportion of electronegative constituents of a substance,
   (iii) may transfer an electron to another substance or group of substances.

30. The most common oxidation state of oxygen in compounds is -2. This is best explained as due to
   (i)   3 electrons in its outermost orbit
   (ii) 4 electrons in its outermost orbit
   (iii) 2 electrons in its outermost orbit
   (iv) 6 electrons in its outermost orbit.

31. Which one of the following statements is true of aluminium in the thermite reaction ?
   (i)   It gains electrons and is oxidised.
   (ii) It gains electrons and is reduced.
   (iii) It loses electrons and is oxidised.
   (iv) It loses electrons and is reduced.

32. In which one of the following compounds of chlorine is $+1$ oxidation state ?
   (a) HCl (b) $HClO$ (c) $HClO_2$ (d) Cl_2O.

33. Oxidation state of chlorine in potassium perchlorate is
   (a) $+1$ (b) -1 (c) $+7$ (d) $+5$.

(B) Fill in the blanks :
   1. Oxidation state of chlorine in Cl_2 is............
   2. In oxidation the oxidation number of the substance............
   3. Electrons are.........in oxidation whereas they are............in reduction.

Ans. (A) 1. (iii), 2. (ii), 3. (i), 4. (iv), 5. (i), 6. (ii), 7. (ii), 8. (ii),
9. (ii), 10. (iii), 11. (iii), 12. (i), 13. (iv), 14. (iv), 15. (i), 16. (i), 17. (i),
18. (iii), 19. (v), 20. (iv), 21. (iv), 22. (iii), 23. (i), 24. (ii), 25. (i), 26. (i),
27. (ii), 28. (iii), 29. (iii), 30. (iv), 31. (iii), 32. (b), 33. (c),
   (B) 1. 0,   2. increases,   3. lost gained.

□ □ □

VALENCY, ATOMIC WEIGHT AND EQUIVALENT WEIGHT

Valency—It is seen that atoms of different elements combine with one or more atoms of hydrogen. This is because they possess an ability to do so. This ability is called their **combining capacity** or **valency**.

The valency of an element is its capacity for combining with other elements and is measured by the number of Hydrogen or Chlorine atoms which combine with or are displaced by one atom of the element.

Examples : (i) Consider the following compounds :

$$HCl, H_2O, NH_3, CH_4$$
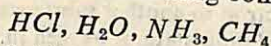
According to the definition of valency, the valencies of Cl, O, N and C in the above compounds are 1, 2, 3 and 4 respectively.

(ii)
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
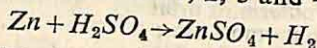
In this reaction, two atoms of H are displaced from H_2SO_4 by one atom of Zn. Hence, the valency of Zinc is 2.

(iii) Now, take the following compounds :

$$NaCl, BaCl_2, BCl_3, SnCl_4$$
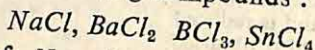
The valencies of Na, Ba, B and Sn will be 1, 2, 3 and 4 respectively.

Different elements possess different capacities for combining with hydrogen. For example, oxygen atom can combine with two atoms of hydrogen but a chlorine atom can hold one hydrogen atom only. Hence, oxygen has combining power twice that of chlorine. The valency of Oxygen is thus 2.

Classification of Elements according to their Valencies :

Monovalent	Divalent	Trivalent	Tetravalent	Pentavalent	Hexavalent
H	O	B	C	N	S
F	Ca	Al	Si	P	
Cl	Sr	Au(ic)	Sn(ic)		
Br	Ba	Bi			
I	Zn	Fe(ic)			
K	Mg				
Na	Cu(ic)				
Hg(ous)	Hg(ic)				
Cu(ous)	Fe(ous)				
Ag	Sn(ous)				
	Pb				

Classification of Radicals according to their valency :

Monovalent   : NH_4^-, OH, NO_2^-, NO_3^-

Divalent   : SO_3^{2-}, SO_4^{2-}, CO_3^{2-}

Trivalent   : PO_4^{3-}, PO_3^{3-}, BO_3^{3-}, $[Fe(CN)_6]$

                   (ferricyanide)

Tetravalent   : $[Fe(CN)_6]^{4-}$

                   (ferrocyanide)

Definition of Valency from Electronic Configuration :

The electrons in the outermost shell of the atom of an element are known as **valence electrons**, for they determine the valency of the element.

Example : $Na(11)$ $1s^2 2s^2 2p^6 3s^1$

                   V. E. = 1

                   ∴ Valency of $Na = 1$.

Variable valency—Some elements exhibit more than one valency. For example, copper forms two types of chlorides represented by the formula Cu_2Cl_2 and $CuCl_2$. Similarly, the oxides of copper are represented as Cu_2O and CuO. From these it is seen that copper has two valencies 1 and 2. Likewise, iron also has two valencies, 2 and 3. Besides, a large number of other elements show variable valency.

Equivalent Weight

The equivalent weight of an element is that weight of it which can combine with or displace from a compound 1 part by weight of Hydrogen or 8 parts by weight of Oxygen or 35·5 parts by weight of Chlorine.

Thus, in **HCl** we have

1 part by weight of Hydrogen combines with 35·5 parts by weight of Chlorine giving 36·5 parts by weight of HCl.

∴ Equivalent weight of chlorine = 35·5.

In methane (CH_4), we have

4 parts by wt. of Hydrogen combine with 12 parts by wt. of C, hence, 1 part by wt. of H combines with $\frac{12}{4} = 3$ parts by wt. of C. Hence, Equivalent weight of Carbon = 3.

The equivalent weight is the ratio of the weight of the element to the weight of hydrogen combined with or replaced by that weight of the element. Hence, it is a pure number.

Variable Equivalent weights—When an element combines with H, O, Cl etc. giving in each case only one compound, the equivalent weight of the element remains fixed. But, in case, the element forms more than one compound, the equivalent weight changes. For example, Cu combines with O forming two oxides, Cu_2O and CuO. In Cu_2O, 16 parts by wt. of oxygen is combined with $2 \times 63·5$

parts by weight of copper. Hence, for 8 parts by wt. of oxygen, the wt. of copper required will be 63·5 parts by wt. The equivalent weight of copper is, thus, 63·5.

In CuO, 16 parts by wt. of oxygen is combined with 63·5 parts by weight of copper. Hence, for 8 parts by wt. of oxygen, wt. of

copper required $= \dfrac{63·5}{2} = 31·75$ parts by wt. The equivalent weight

of copper is, then, 31·75.

Gram-equivalent—The equivalent weight when expressed in gram is called **Gm-equivalent**. For example, equivalent weight of Magnesium is 12. Hence, 12 g of Mg stands for 1 gm-equivalent of Mg.

Thus, $\text{Gm-Equivalent} = \dfrac{\text{Wt. in Gram}}{\text{Equivalent weight}}$.

Determination of Equivalent Weights

(A) Of Non-metals

1. By direct union with Hydrogen.
2. By oxide formation.
3. By combination with chlorine.

(B) Of Metals

1. Hydrogen displacement Method.
2. By Oxide formation.
3. By combination with Chlorine.
4. Replacement of one metal by another.
5. Electrolytic Method.
6. Acid-base Titration Method.

Equivalent weight of Non-Metals

1. By direct union with Hydrogen—The equivalent weight of Oxygen may be obtained by this method.

A weighed bulb tube containing pure and dry cupric oxide (CuO) is taken. One end of this tube is connected to a H_2 generator. The other end is connected to a weighed U-tube containing fused $CaCl_2$. A current of H_2 is now passed through the apparatus. When all air inside the apparatus has been expelled by H_2, the bulb is heated. CuO combines with H_2 forming Cu, which is retained in the bulb, and H_2O is absorbed in the U-tube.

When the reaction is over, the apparatus is cooled continuing the passage of H_2. U-tube and the bulb tube are now detached and weighed separately.

Results : Let the initial weight of the bulb $= w_1$ g

Final weight of the bulb $= w_2$ g.

$\therefore$ Wt. of Oxygen $= (w_1 - w_2)$ g.

Initial wt. of the U-tube $= w_3$ g

Final wt. of the U-tube $= w_4$ g

$\therefore$ wt. of water $= (w_4 - w_3)$ g

$\therefore$ wt. of Hydrogen $= (w_1 - w_3) - (w_1 - w_2)$ g.

$$\therefore \quad \text{Equivalent wt. of Oxygen} = \frac{(w_1 - w_2)}{(w_4 - w_3) - (w_1 - w_2)}.$$

Equivalent weight of Metals

1. Hydrogen displacement Method :

Theory : Some metals dissolve in dilute acids and liberate Hydrogen gas.   The volume of H_2 liberated is measured.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
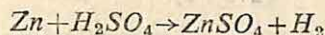
From the known weight of metal and the weight of Hydrogen being known, equivalent weight of the metal is calculated.

Procedure : A small piece of pure Zinc (about 0·08 g) is weighed out in a watch glass and placed at the bottom of a beaker of water.   The metal is covered with a conical funnel in such a way that the stem of the funnel remains comple- tely dipped in water.   A gra- duated tube is now filled with water and inverted over the stem of the funnel so that the stem is well inside the tube (see the given fig.).

Now, moderately 'concen- trated H_2SO_4 is added to the water in beaker.   A few drops of $CuSO_4$ solution is also added. As pure Zn metal reacts very slowly in the begin- ning. the addition of $CuSO_4$ solution hastens the reaction. H_2 gas is evolved and collects in the graduated tube by the downward displacement of water.
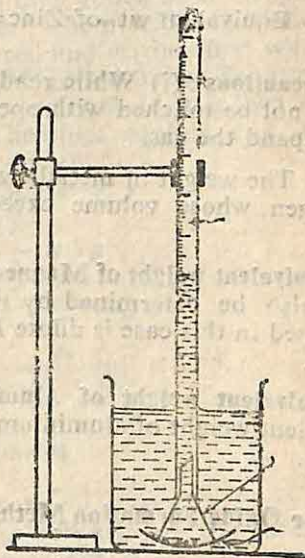
After Zinc has completely dissolved, the mouth of the graduated tube is carefully closed with the thumb inside water. It is then taken out as such and plunged into a bell jar full of water. The surface

of water is brought to the same level inside and outside the tube by holding the tube with a piece of paper as shown in fig. Page 115.

The volume of Hydrogen is read. Room temperature and atmospheric pressure are also noted.

Results : Let the wt. of watch glass be w. g
    wt. of watch glass+Zinc=w_2 g
∴   wt. of Zinc=$(w_2 - w_1)$ g.
Volume of H_2 evolved=V ml
Room temperature=$t°C = (273+t)$ K
Atmospheric pressure=P mm
Aqueous tension at $t°C$=f mm.
∴   Pressure due to $H_2 = (P-f)$ mm
Let V ml of H_2 occupy V_1 ml at N.T.P.

$$\therefore \quad \frac{(P-f) \times V}{(273+t)} = \frac{760 \times V_1}{273}$$

or
$$V_1 = \frac{273 \times (P-f) \times V}{760 \times (273+t)} = x \text{ ml (say)}.$$

∴ Wt. of H_2 at N.T.P.=$(0·00009 \times x)$ g.

∴ Equivalent wt. of Zinc=$\dfrac{(w_2 - w_1)}{0·00009 \times x}$.

Precautions : (i) While reading the volume, the graduated tube should not be touched with open hand. The warmth of the hand will expand the gas.

(ii) The weight of metallic zinc must be such that may not evolve hydrogen whose volume exceeds the capacity of the graduated tube.

Equivalent weight of Magnesium : The equivalent weight of Mg may also be determined by Hydrogen displacement method. The acid used in this case is dilute H_2SO_4. But $CuSO_4$ solution is not added.

Equivalent weight of Aluminium : In the determination of the equivalent weight of aluminium dilute HCl is used in place of dil. H_2SO_4.

2. The Oxide Formation Method :

Equivalent weight of Copper : A porcelain crucible with its lid is thoroughly washed and dried to constant weight. A piece of pure copper is weighed in it. Conc HNO_3 is now added to it dropwise till copper dissolves. The crucible is kept covered with the lid during the reaction. The solution is evaporated on a water bath. Care is taken that no copper is lost by spurting. The residue left behind is

strongly heated. $Cu(NO_3)_2$ is thus completely converted into black CuO.

$$2Cu(NO_3)_2 \rightarrow 2CuO + 2NO_2 + 3O_2$$

The crucible is now cooled in a desiccator and weighed. The process of heating, cooling in the desiccator and weighing is continued till the final weight becomes constant.

Calculation : Wt. of crucible + lid = w_1 g

wt. of crucible with lid + copper = w_2 g.

∴ wt. of copper = $(w_2 - w_1)$ g.

Let the final constant weight be w_3 g.

∴ Wt. of oxygen = $w_3 - (w_2 - w_1)$ g.

∴ Equivalent weight of copper = $\dfrac{(w_2 - w_1)}{w_3 - (w_2 - w_1)} \times 8$.

N. B.—The same method is adopted for the equivalent weight of Mg, Sn, Pb etc.

3.   By Combination with Chlorine :

Equivalent weight of Silver—A piece of clean and pure silver is weighed in a porcelain crucible with its lid. It is then dissolved in dilute HNO_3 in such a way that the solution is only slightly acidic. The solution is boiled. Pure HCl is then added to it dropwise till precipitation of $AgCl$ is complete. The precipitate is allowed to settle for some time. It is then filtered and washed first with water containing a little HNO_3 and finally with water only. The precipitate is dried at 100°C in an air oven and then cooled. It is then weighed in a weighing tube. The process of heating, cooling and weighing is continued till the final weight is constant.

Results : Let the wt. of crucible + lid be w_1 g.

Wt. of crucible with lid + Ag = w_2 g.

∴   Wt. of Ag = $(w_2 - w_1)$ g

Wt. of $AgCl$ = w_3 g

∴   Wt. of chlorine = $w_3 - (w_2 - w_1)$ g

∴   Eq. wt. of silver = $\dfrac{w_3}{w_3 - (w_2 - w_1)} \times 35 \cdot 5$.

4.   By replacement of one metal by another :

Theory : A more electropositive metal displaces a less electropositive metal from a solution of a soluble salt of the latter. For example, when iron or zinc is immersed in a solution of copper sulphate, copper is precipitated out of the solution.

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu \downarrow$$
$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu \downarrow$$
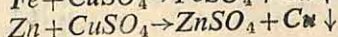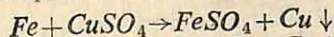
The weight of the metal which displaces and the weight of the

metal which is displaced are found to be in the ratio of their equivalent weights.

$$\frac{\text{weight of the metal } A}{\text{weight of the metal } B} = \frac{\text{Equivalent weight of } A}{\text{Equivalent weight of } B}.$$

So, determining the weights of A and B and knowing equivalent weight of one of them, the equivalent weight of the other can be calculated.

5. Electrolytic method :

The determination of equivalent weight by this method is based on **Faraday's Second Law of Electrolysis.** According to this law, when the same quantity of electricity is passed through different electrolytes, the substances liberated are in the ratio of their chemical equivalents.

If a current is passed through solutions of salts of metals A and B, connected in series, then

$$\frac{\text{Wt. of } A \text{ liberated}}{\text{Wt. of } B \text{ liberated}} = \frac{\text{Equivalent wt. of } A}{\text{Equivalent wt. of } B}.$$

If the equivalent weight of one of them is known, the equivalent weight of the other can be calculated.

Further, Electrochemical equivalent $= \dfrac{\text{Chemical Equiv.}}{96500}$

or $\qquad$ Equiv. wt. $= \text{E.C.E.} \times 96500.$

Again $\qquad$ $\text{E.C.E.} = \dfrac{\text{wt. of substance liberated}}{\text{current (amp.)} \times \text{time (sec.)}} = \dfrac{W}{c \times t}$

$\therefore \qquad$ Eq. wt. $= \dfrac{W}{c \times t} \times 96500.$

Solved Problems

1. 0·164 g of a metal when dissolved in HCl evolves 31 ml of Hydrogen at N.T.P. Calculate the equivalent weight of the metal.

Solution : Wt. of 31 ml of Hydrogen at N.T.P. $= 31 \times 0 \cdot 00009$ g
$$= 0 \cdot 00279 \text{ g.}$$

$\therefore$ Equivalent wt. of the metal $= \dfrac{\text{wt. of the metal}}{\text{wt. of } H_2}$

$$= \frac{0 \cdot 164}{0 \cdot 00279} = 58 \cdot 78.$$

2. 3·36 g of Zinc evolves 1210 ml of Hydrogen from dilute sulphuric acid at 10·7°C and 747·8 mm pressure. Determine the equivalent weight of the metal, if the aqueous tension at 10·7°C is 9·8 mm.

Solution :   Wt. of Zinc = 3·36 g.
Volume of Hydrogen = 1210 ml.
Temperature = 10·7°C = (273 + 10·7) = 283·7 K.
Pressure = 747·8 mm.
Aqueous tension at 10·7°C = 9·8 mm.
∴ Pressure of Hydrogen = 747·8 − 9·8 = 738 mm.
Let the volume of Hydrogen at N.T.P. be V ml.

∴ $$\frac{760 \times V}{273} = \frac{738 \times 1210}{283\cdot7}$$

or $$V = \frac{738 \times 1210 \times 273}{760 \times 283\cdot7} = 1130\cdot65 \text{ ml.}$$

∴ Wt. of Hydrogen = 1130·65 × 0·00009 g = 0·10176 g.

∴ Equivalent wt. of metal = $\dfrac{\text{wt. of metal}}{\text{wt. of Hydrogen}}$

$$= \frac{3\cdot36}{0\cdot10176} = 33\cdot0.$$

3. What is the equivalent weight of a metal 24 g of which evolve from an acid 22·4 litre of Hydrogen at N.T.P. ?

Solution : 22·4 litre of H_2 at N.T.P. = (0·09 × 22·4) g = 2·016 g
Wt. of metal = 24 g.

∴ Equivalent wt. of metal = $\dfrac{24}{2\cdot016} = 12.$

4. On heating 0·8567 g of copper oxide in a current of Hydrogen the resulting copper weighed 0·6842 g. What is the equivalent weight of copper ?

Solution : Wt. of copper oxide = 0·8567 g
Wt. of copper = 0·6842 g
∴ Wt. of oxygen = (0·8567 − 0·6842) g
= 0·1725 g.

∴ Equivalent wt. of copper = $\dfrac{\text{wt. of copper}}{\text{wt. of oxygen}} \times 8$

$$= \frac{0\cdot6842}{0\cdot1725} \times 8 = 31\cdot73.$$

5. The bromide of a metal contains 90% Bromine. The oxide of the same metal contains 47% of Oxygen. What is the equivalent weight of Bromine ?

Solution : Let the oxide of the metal be 100 g.

∴   Wt. of metal $= 100 - 47 = 53$ g.

∴   Wt. of oxygen $= 47$ g

∴   Equivalent weight of the metal $= \frac{53}{47} \times 8 = 9.02$.

Again, let the bromide of the metal weigh 100 g.

∴   Wt. of Bromine $= 90$ g.

∴   Wt. of the metal $= 100 - 90 = 10$ g.

Now, ∵   10 g of the metal combines with 90 g of Bromine,

∴   9.02 g of the metal combines with $\dfrac{90 \times 9.02}{10}$ g of Bromine

$$= 81.18 \text{ g of Bromine.}$$

∴   Equivalent weight of Bromine $= 81.18$.

6.   1.201 g of Zinc gave 1.497 g of Zinc oxide on treatment with nitric acid and subsequent ignition.

In a second experiment 0.543 g of Zinc precipitated 0.527 g of copper from a solution of copper sulphate.

Calculate the equivalent weight of Copper.

Solution :

Wt. of Zinc $= 1.201$ g.

Wt. of Zinc oxide $= 1.497$ g.

∴   Wt. of Oxygen $= (1.497 - 1.201)$ g

$$= 0.296 \text{ g.}$$

∴   Equivalent wt. of Zinc $= \dfrac{\text{wt. of Zinc}}{\text{wt. of Oxygen}} \times 8$

$$= \frac{1.201}{0.296} \times 8 = 32.46.$$

In the second experiment :

Let the equivalent weight of Copper be E.

∴ $\dfrac{\text{Wt. of Copper displaced}}{\text{Wt. of Zinc}} = \dfrac{\text{Equivalent wt. of Copper}}{\text{Equivalent wt. of Zinc}}$

or $\dfrac{0.527}{0.543} = \dfrac{E}{32.46}$

or $E = \dfrac{0.527 \times 32.46}{0.543} = 31.5$

i.e.,   Equivalent wt. of Copper $= 31.5$.

7.   The chloride of a metal M contains 47.23% of the metal. 1.00 g of this metal displaced from a compound 0.88 g of another metal N. Find the equivalent weights of M and N.

Solution : Let the weight of the chloride of metal M be 100 g.

$\therefore$ Wt. of metal $M = 47 \cdot 23$ g.

$\therefore$ Wt. of chlorine $= 100 - 47 \cdot 23 = 52 \cdot 77$ g.

$\therefore$ Equivalent wt. of the metal $M = \dfrac{\text{wt. of metal}}{\text{wt. of chlorine}} \times 35 \cdot 5$

$$= \frac{47 \cdot 23}{52 \cdot 77} \times 35 \cdot 5 = 31 \cdot 77.$$

Wt. of metal N displaced $= 0 \cdot 88$ g.

$\therefore$ $\dfrac{\text{Equivalent wt. of } M}{\text{Equivalent wt. of } N} = \dfrac{\text{wt. of } M}{\text{wt. of } N}$

or $\dfrac{31 \cdot 77}{E} = \dfrac{1}{0 \cdot 88},$ or $E = \dfrac{31 \cdot 77 \times 0 \cdot 88}{1} = 27 \cdot 96$

i.e.,   Equivalent wt. of metal $N = 27 \cdot 96$.

8. Two cells, one containing $CuSO_4$ solution and the other $AgNO_3$ solution, are joined in the same electric circuit. It is found that $0 \cdot 106$ g of Cu is deposited in the same time as $0 \cdot 3597$ g of Ag. If the equivalent weight of Cu is $31 \cdot 8$, calculate the equivalent weight of Ag.

Solution : $\dfrac{\text{Wt. of } Ag \text{ deposited}}{\text{Wt. of } Cu \text{ deposited}} = \dfrac{\text{Eq. wt. of } Ag}{\text{Eq. wt. of } Cu}$

or $\dfrac{0 \cdot 3597}{0 \cdot 106} = \dfrac{E}{31 \cdot 8}$ $(E = \text{Eq. wt. of } Ag)$

or $E = \dfrac{0 \cdot 3597 \times 31 \cdot 8}{0 \cdot 106} = 107 \cdot 91.$

9. What weight of silver will be obtained when 3 g of copper are left in excess $AgNO_3$ solution ? (Eq. wt. of $Ag = 108$, and that of $Cu = 31 \cdot 7$.)

Solution : $\because$ $31 \cdot 7$ g of Cu liberate 108 g of Ag,

$\therefore$ 3 g of Cu liberate $\dfrac{108 \times 3}{31 \cdot 7}$ g of $Ag = 10 \cdot 2$ g of Ag.

10. $0 \cdot 5$ g of calcium chloride gave $1 \cdot 2925$ g of silver chloride on treatment with silver nitrate solution. Calculate the equivalent weight of silver, those of calcium and chlorine being 20 and 35·5 respectively.

Solution :

$\dfrac{\text{Wt. of the salt taken}}{\text{Wt. of the salt precipitated}} = \dfrac{\text{Eq. wt. of metal} + \text{Eq. wt. of acid radical}}{\text{Eq. wt. of metal} + \text{Eq. wt. of acid radical}}$

or
$$\frac{0\cdot5}{1\cdot2925} = \frac{20+35\cdot5}{E+35\cdot5} \quad (E = \text{Eq. wt. of } Ag)$$

or
$$\frac{0\cdot5}{1\cdot2925} = \frac{55\cdot5}{E+35\cdot5} \quad \text{or} \quad E = 108.$$

Atomic Weight

Definitions :

1. The atomic weight of an element is the smallest weight of it present in the molecular weights of its compounds.

2. Using the weight of a hydrogen atom as standard, the atomic weight is defined as :

The atomic weight of an element is a number which shows how many times the weight of one atom of the element is greater than the weight of one atom of hydrogen.

i.e., Atomic weight of an element $= \dfrac{\text{wt. of 1 atom of the element}}{\text{wt. of 1 atom of Hydrogen}}$.

3. A special unit is now applied to express the weights of atoms. This unit is called the atomic mass unit (a.m.u.). It is defined as exactly 1/12th the mass or weight of a C^{12} atom. It is designated by the symbol μ. Thus, the weight of the C^{12} atom is exactly 12μ. On this basis the atomic weight may now be defined as follows :

The atomic weight of an element is a ratio of the weight of one atom of the element to 1/12th the weight of one C^{12} atom.

i.e., atomic weight of an element $= \dfrac{\text{wt. of 1 atom of the element}}{\text{1/12th the wt. of } C^{12} \text{ atom}}$.

Thus, the weight of the Na^{23} atom is $22\cdot9898\mu$.

Gram-atom—The gram-atom of an element is its atomic weight expressed in gram. Thus, 1 gm-atom of Oxygen stands for 16 g of Oxygen (at. wt. of Oxygen $= 16$).

i.e., Gram-atom $= \dfrac{\text{wt. of the element in gram}}{\text{At. wt. of the element}}$.

A mole of atoms is often called a gm-atom.

Relation between Valency, Equivalent weight and Atomic weight :

Let the valency, equivalent weight and atomic weight of an element be V, E and A respectively. According to the definition of valency,

V atoms of Hydrogen combine with 1 atom of the element

i.e., V gm-atoms of Hydrogen combine with 1 gm-atom of the element

i.e., V g of Hydrogen combine with A g of the element,

$\therefore$ 1 g of Hydrogen combines with $\frac{A}{V}$ g of the element.

Thus, equivalent wt. (E) of the element $= A/V$;   or $E = \frac{A}{V}$

i.e., Atomic weight = Equivalent weight × Valency.

Determination of Atomic Weights :

The atomic weights of elements are generally determined by the following methods :

1. From the equivalent weight of the element.
2. Cannizzaro's Method.
3. From Dulong and Petit's law.
4. From Mitscherlich's law of Isomorphism.
5. With the aid of the Periodic Table.

1. From the Equivalent weight of the Element—The scheme followed in this method is as follows :

(i) The Eq. wt. of the element is determined cautiously.

(ii) An approximate atomic weight of the element is determined following Dulong and Petit's law.

(iii) The valency of the element is now calculated by the formula.

Approx. at. wt. = Eq. wt. × valency.

The valency is always a whole number.

(iv) The exact atomic weight is now worked out as,

At. wt. = Eq. wt. × Valency.

2. Cannizzaro's Method—This method is based on the fact that **the smallest weight of the element present in the molecular weights of its various compounds is the atomic weight of the element.** The scheme of this method is as follows :

(i) The vapour densities of a large number of its gaseous or volatile compounds are determined.

(ii) The molecular weight is now calculated as,

Molecular wt. = 2 × vapour density.

(iii) Each compound is now analysed to find the exact weight of the element present in a molecule of the compound.

(iv) From the data at disposal, the smallest weight of the element present in the molecular weights of a large number of its compounds is sorted out. This smallest weight represents the atomic weight of the element.

Example :

Atomic Weight of Carbon

Compound	Vapour density	Molecular weight	Weight of Carbon in the molecular wt. of the compound
Carbon dioxide	22	$2 \times 22 = 44$	12 g
Carbon monoxide	14	$2 \times 14 = 28$	12 g
Methane	8	$2 \times 8 = 16$	12 g
Ethane	15	$2 \times 15 = 30$	24 g
Acetone	29	$2 \times 29 = 58$	36 g
Benzene	39	$2 \times 39 = 78$	72 g

Thus, 12 g is the smallest wt. of Carbon present in the molecular weights of its compounds. Hence, the atomic weight of Carbon = 12.

3. **From Dulong and Petit's Law**—Dulong and Petit's law may be stated as :

The product of the atomic weight and the specific heat of all solid elements is a constant, and is equal to 6·4 approximately.

Thus, At. wt. × Sp. heat = 6·4 (approx.).

This constant value is known as the **atomic heat.**

In order to determine the exact atomic weight of an element the following scheme is adopted :

(i) The specific heat of the solid element is determined accurately.

(ii) Approximate atomic weight is now found out by the relation,

$$\text{At. wt.} = \frac{6 \cdot 4}{\text{Sp. heat}}.$$

(iii) The equivalent wt. of the solid element is determined accurately.

(iv) The valency of the element is then determined by the relation,

$$\text{Valency} = \frac{\text{Approx. at. wt.}}{\text{Eq. wt.}}.$$

This value of valency is changed to the nearest whole number to get the actual value of valency.

(v) Now, exact at. wt. = Eq.wt. × Valency.

Demerits of this method : (i) It is applicable to solid elements only.

(ii) It does not apply to Carbon, Boron, Silicon etc.

4. From Mitscherlich's Law of Isomorphism—The Law of Isomorphism may be stated as follows :

Two compounds, crystallising in the same form and composed of the same number of atoms combined in a similar manner, are said to be isomorphous with each other.

Example :

$ZnSO_4.7H_2O$	and	$MgSO_4.7H_2O$
(Zinc sulphate)		(Magnesium sulphate)
$K_2SO_4.Al_2(SO_4)_3.24H_2O$	and	$Cr_2(SO_4)_3.Al_2(SO_4)_3.24H_2O$
(Potash alum)		(Chrome alum)
$KClO_4$	and	$KMnO_4$
(Potassium perchlorate)		(Potassium permangante)
K_2CrO_4	and	K_2SO_4
(Potassium chromate)		(Potassium sulphate)

If we consider two isomorphous compounds, one made up of elements of known atomic weights and the other containing an element of unknown atomic weight, the latter can be compared with that of the element it replaces. Thus, two cases arise :

(i) Let there be two elements A and B combining with a fixed weight of other elements in their compounds. The weights of A and B will then be in the ratio of their atomic weights.

$$\text{i.e., } \frac{\text{wt. of } A}{\text{wt. of } B} = \frac{\text{At. wt. of } A}{\text{At. wt. of } B}.$$

(ii) The valencies of the two elements replacing each other in isomorphous compounds will be the same.

5. From Periodic Table—The atomic weights of elements can also be known from the Periodic Table.

Solved Problems

1. The Eq. wt. of Magnesium is found to be 12·16. Its approximate at. wt. determined by other methods is 23. Calculate the exact atomic weight of Magnesium.

Solution :   Valency of $Mg = \dfrac{23}{12·16} = 1·89.$

But valency cannot be a fractional number. It must be a whole number. Hence, the valency will be 2.

$\therefore$ Exact At. wt. = Valency × Eq. wt.
= 2 × 12·16 = 24·32.

2. The vapour densities of a number of compounds of phosphorus and the percentage of phosphorus in these compounds were

found to be as follows :

Compound	Vapour density	% of Phosphorus
Phosphoric oxide	150	43·7
Phosphorus oxide	110	56·4
Phosphorus trichloride	70	22·5
Phosphorus pentachloride	63	24·6
Phosphorus oxychloride	77	20·2

Calculate the probable atomic weight of Phosphorus.

Solution :

Compound	V.D.	Mole. wt.	Wt. of P in one gram molecular wt.	Smallest wt. of Phosphorus
Phosphoric oxide	150	300	$\frac{43\cdot7}{100} \times 300 = 131\cdot1$	
Phosphorus oxide	110	220	$\frac{56\cdot4}{100} \times 220 = 124\cdot08$	
Phosphorus trichloride	70	140	$\frac{22\cdot5}{100} \times 140 = 31\cdot50$	31·108
Phosphorus pentachloride	63	126	$\frac{24\cdot6}{100} \times 126 = 30\cdot996$	
Phosphorus oxychloride	77	154	$\frac{20\cdot2}{100} \times 154 = 31\cdot108$	

∴   Probable At. wt. of $P = 31\cdot108$.

3. The chloride of a metal was found to contain 47·22% of the metal. Its specific heat is 0·094. What is its exact At. wt. ?

Solution : Let the wt. of the chloride of the metal be 100 g.

∴   Wt. of metal = 47·22 g

Wt. of chlorine = 100 − 47·22 = 52·78 g.

∴   Eq. wt. of metal = $\frac{47\cdot22}{52\cdot78} \times 35\cdot5 = 31\cdot76$.

$$\text{Approx. At. wt.} = \frac{6 \cdot 4}{\text{Sp. heat}} = \frac{6 \cdot 4}{0 \cdot 094} = 68 \cdot 08.$$

$$\therefore \quad \text{Valency} = \frac{\text{At. wt.}}{\text{Eq. wt.}} = \frac{68 \cdot 08}{31 \cdot 76} = 2 \cdot 1.$$

But valency is always the nearest whole number.
∴ Valency of the metal = 2
∴ Exact At. wt. = valency × Eq. wt.
$$= 2 \times 31 \cdot 76 = 63 \cdot 52.$$

4. The bromide of a metal contains 81·08% Bromine. The specific heat of the metal is 0·11. Calculate the Equivalent weight, Atomic weight and Valency of the metal. ($Br = 80$).

Solution : Let the wt. of the bromide be 100 g.
∴ Wt. of Bromine = 81·08 g
and wt. of the metal = 100 − 81·08 = 18·92 g
∴ 81·08 g of Bromine combine with 18·92 g of metal,

$$\therefore \quad 80 \text{ g} \qquad ,, \quad ,, \quad ,, \quad \frac{18 \cdot 72 \times 80}{81 \cdot 08} \text{ g ,,}$$

$$= 18 \cdot 66 \text{ g} \qquad ,,$$

i.e., Eq. wt. of the metal = 18·66,
Sp. heat of the metal = 0·11.

∴ From Dulong and Petit's law,

$$\text{Approx. At. wt.} = \frac{6 \cdot 4}{0 \cdot 11} = 58 \cdot 18,$$

$$\text{Equivalent wt.} = 18 \cdot 66;$$

$$\therefore \quad \text{Valency} = \frac{58 \cdot 18}{18 \cdot 66} = 3 \cdot 12.$$

∴ Correct valency = 3.
∴ Correct atomic weight = 3 × 18·66 = 55·98.

5. A sample of metal chloride weighing 0·22 g required 0·51 g of silver nitrate to precipitate the chloride completely. The specific heat of the metal is 0·057. Find out the molecular formula of the chloride if the symbol of the metal is M. (**I.I.T. Admission Test 1976**)

Solution : Let the equivalent weight of the metal be E.
∴ Eq. wt. of the chloride = $(E + 35 \cdot 5)$.
Eq. wt. of Silver nitrate = Eq. wt. of Ag + Eq. wt. of NO_3^- ion
$$= 108 + 62 = 170.$$

$$\therefore \quad \frac{E + 35 \cdot 5}{170} = \frac{\text{wt. of metallic chloride}}{\text{wt. of } AgNO_3 \text{ needed}} = \frac{0 \cdot 22}{0 \cdot 51}$$

or $0.51(E+35.5) = 170 \times 0.22$
or $0.51E + 35.5 \times 0.51 = 170 \times 0.22$
or $0.51E = 19.295;$

$\therefore$ $E = \dfrac{19.295}{0.51} = 37.83$

i.e.,   Eq. wt. of the metal $= 37.83$,
      Sp. heat of the metal $= 0.057$.

$\therefore$ Approx. at. wt. $= \dfrac{6.4}{0.057} = 112.3$.

$\therefore$ Valency $= \dfrac{112.3}{37.83} = 2.97$.

$\therefore$ Correct valency $= 3$.
$\therefore$ Molecular formula of the chloride : MCl_3.

6. 0.200 g of anhydrous chloride of an element on treatment with sulphuric acid gave 0.263 g of anhydrous sulphate. Find the eq. wt. and at. wt. of the metal, if its sp. heat is 0.64.

Solution : Let the Eq. wt. of the metal be E.
$\therefore$ Eq. wt. of the chloride of metal $= (E+35.5)$.
    Eq. wt. of sulphate ion $= 48$.
$\therefore$ Eq. wt. of metallic sulphate $= (E+48)$.

$\therefore$ $\dfrac{E+35.5}{E+48} = \dfrac{\text{wt. of anhydrous chloride}}{\text{wt. ot anhydrous sulphate}} = \dfrac{0.2}{0.263}$

or $0.263(E+35.5) = 0.2(E+48)$
or $0.263E + 0.263 \times 35.5 = 0.2E + 0.2 \times 48$
or $0.263E + 9.336 = 0.2E + 9.6$

or $0.063E = 0.264;$ $\therefore$ $E = \dfrac{0.264}{0.063} = 4.19$.

i.e.,   Eq. wt. of the metal $= 4.19$.
      Sp. heat $= 0.64$.

       Approx. At. wt. $= \dfrac{6.4}{0.64} = 10$.

$\therefore$ Valency $= \dfrac{10}{4.19} = 2.38$.

$\therefore$ Correct valency $= 2$.
$\therefore$ Correct At. wt, of the metal $= 2 \times 4.19 = 8.38$.

7. A sample of metal oxide weighing 6.50 g is decomposed quantitatively to give 6.251 g of the metal. The sp. heat of the metal is 0.0332 cal/g. Calculate the exact atomic weight of the metal and the empirical formula of the oxide.

Solution : Wt. of the oxide $= 6·50$ g

Wt. of the metal $= 6·251$ g

$\therefore$ Wt. of oxygen $= 6·50 - 6·251 = 0·249$ g.

$\therefore$ Eq. wt. of the metal $= \dfrac{6·251}{0·249} \times 8 = 200·83$ g.

Sp. heat of the metal $= 0·0332$

$\therefore$ Approx. at. wt. $= \dfrac{6·4}{0·0332} = 192·77$

$\therefore$ Valency $= \dfrac{192·77}{200·83} = 0·96$

$\therefore$ Correct valency $= 1$

$\therefore$ Correct at. wt. $= 1 \times 200·83 = 200·83$

$\therefore$ Empirical formula of oxide : M_2O

8. The chloride of an element contains $75·85\%$ of chlorine and the density of its vapour is 91 times that of hydrogen. What is the formula of the compound and the atomic weight of the element ? $(Cl = 35·5)$

Solution :   Let the wt. of the metallic chloride be 100 g.

$\therefore$ Wt. of chlorine $= 75·85$ g

Wt. of the metal $= 100 - 75·85 = 24·15$ g

$\therefore$ Eq. wt. of the metal $= \dfrac{24·15}{75·85} \times 35·5 = 11·3$

Vapour density $= 91$

$\therefore$ Molecular weight $= 2 \times 91 = 182$

Let the valency of the metal be x.

$\therefore$ At. wt. of the metal $= 11·3 \times x$

Formula of the metallic chloride, MCl_x

$\therefore$ Formula weight of the metallic chloride,

$= 11·3x + 35·5x = 46·8x;$ $\therefore$ $46·8x = 182$

or

$$x = \dfrac{182}{46·8} = 3·88$$

$\therefore$ Correct valency $= 4$

$\therefore$ Formula of the compound : MCl_4

$\therefore$ Correct At. wt. $= 4 \times 11·3 = 45·2$

9. On dissolving $2·00$ g of a metal in sulphuric acid $4·51$ g of the metal sulphate was formed. The specific heat of the metal is $0·057$ cal/g. What is the valency of the metal and its exact atomic weight ?   (I.I.T. 1978)

Solution : The eq. wt. of SO_4^{--} radical $= \dfrac{32 + 4 \times 16}{2} = 48$

INTR. CH.-9

∴ 2 g of the metal forms 4·51 g of sulphate,
∴ Wt. of SO_4^{--} = 4·51 − 2·00 = 2·51 g.
i.e.,   2·51 g of the sulphate radical combines with 2 g of metal,

∴ 48 g of the sulphate radical combines with $\dfrac{2 \times 48}{2·51}$ g of metal,

= 38·24 g of metal.
∴   Eq. wt. of metal = 38·24
Applying Dulong and Petit's Law,

$$\text{Approx. At. wt.} = \frac{6·4}{\text{Sp. heat}} = \frac{6·4}{0·057} = 112$$

$$\therefore \text{Valency} = \frac{112}{38·24} = 2·9$$

∴ Correct valency = 3
∴ Exact At wt. = 3 × 38·24 = 114·7.

10. 1 g of a certain metal when dissolved in dil. *HCl* evolves 1242 ml of Hydrogen at N.T.P. The specific heat of the metal is 0·238. Find its equivalent weight, atomic weight and valency.

Solution : Wt. of Hydrogen at N.T.P. = 0·00009 × 1242 g
= 0·11178 g
∴ 0·11178 g Hydrogen is evolved by 1 g of metal,

∴ 1 g Hydrogen is evolved by $\dfrac{1}{0·11178}$ g of metal = 8·94

i.e., Eq. wt. of the metal = **8·94**

Sp. heat of metal = 0·238

$$\therefore \text{Approx. At. wt.} = \frac{6·4}{0·238} = 26·8$$

$$\therefore \text{Valency} = \frac{26·8}{8·94} = 2·9$$

∴ Correct valency = **3**

∴ Correct at. wt. = 3 × 8·94 = **26·82**.

11. A metal forms two oxides, containing respectively 22·2 and 30·0% of Oxygen. Its sp. heat is 0·114. What formula would you assign to them ?

Solution : First Oxide : Let the wt. of the oxide be 100 g.
∴ Wt. of Oxygen = 22·2 g
Wt. of metal = 100 − 22·2 = 77·8 g

$$\therefore \text{ Eq. wt. of the metal} = \frac{77 \cdot 8}{22 \cdot 2} \times 8 = 28 \cdot 03$$

Second Oxide : Let the wt. of the oxide be 100 g.
$$\therefore \text{ Wt. of Oxygen} = 30 \text{ g}$$
$$\text{Wt. of metal} = 100 - 30 = 70 \text{ g.}$$

$$\therefore \text{ Eq. Wt. of the metal} = \frac{70}{30} \times 8 = 18 \cdot 7$$

Sp. heat of the metal $= 0 \cdot 114$

$$\therefore \text{ Approx. At. wt.} = \frac{6 \cdot 4}{0 \cdot 114} = 56 \cdot 1$$

$$\therefore \text{ Valency (in first oxide)} = \frac{56 \cdot 1}{28 \cdot 03} = 2 \text{ (nearest whole number)}$$

$$\text{Valency of metal (in second oxide)} = \frac{56 \cdot 1}{18 \cdot 7} = 3 \text{ (nearest whole number)}$$

As the valency of Oxygen is 2, the formulae will be :
First oxide : M_2O_2, or MO
Second oxide : M_2O_3.

12. The specific heats of the metals M and N are 0·25 and 0·214 respectively and their equivalent weights are 12 and 9 respectively. What would be the formulae of their chlorides ?   (Mith. U. 1978)

Solution : Approx. at. wt. of the metal $M = \frac{6 \cdot 4}{0 \cdot 25} = 25 \cdot 6$

$$\therefore \text{ Valency of metal } M = \frac{25 \cdot 6}{12} = 2 \text{ (nearest whole number)}$$

Now, approx. at. wt. of $N = \frac{6 \cdot 4}{0 \cdot 214}\ 29 \cdot 9$

$$\therefore \text{ Valency of } N = \frac{29 \cdot 9}{9} = 3 \text{ (nearest whole number)}$$

$$\therefore \text{ Formula of the chloride of } M : MCl_2$$
Formula of the chloride of $N : NCl_3$

13. The vapour density of the chloride of a metal is 66·0. In the oxide of the metal the percentage of the metal is 53%. What is the valency and the atomic weight of the metal ? (M U. 1977A.)

Solution : Let the weight of the oxide of the metal be 100 g.
$$\therefore \text{ Wt. of metal} = 53 \text{ g.}$$
$$\text{Wt. of Oxygen} = 100 - 53 = 47 \text{ g}$$

$$\therefore \quad \text{Equivalent weight of the metal} = \frac{53}{47} \times 8 = 9 \cdot 02$$

Molecular weight of the chloride of metal $= 2 \times$ V.D.
$$= 2 \times 66 = 132$$

Let the valency of the metal be x.

∴   Molecular formula of the chloride of metal is MCl_x,

∴   Formula weight $= 9 \cdot 02 \times x + 35 \cdot 5 \times x$

∴ $9 \cdot 02x + 35 \cdot 5x = 132,$ or $44 \cdot 52x = 132$

or $x = \dfrac{132}{44 \cdot 52} = 3$ (nearest whole number)

∴   Exact atomic wt. of the metal $= 3 \times 9 \cdot 02 = 27 \cdot 06$.

14. The weight of oxygen in the oxide of an element is $28 \cdot 6\%$ and the vapour density of its chloride is $55 \cdot 5$. Calculate the atomic weight of the element.

(M. U. 1973 S; R. U. 1977)

Solution :   Let the weight of the oxide be 100 g.

∴   Wt. of Oxygen $= 28 \cdot 6$ g

Wt. of the element $= 100 - 28 \cdot 6 = 71 \cdot 4$g

$$\therefore \quad \text{Equivalent weight of the element} = \frac{71 \cdot 4}{28 \cdot 6} \times 8 = 19 \cdot 91$$

V.D. of the chloride $= 55 \cdot 5$

∴   Molecular weight $= 2 \times 55 \cdot 5 = 111$

Let the valency of the element be x.

∴   At. wt. of the element $= x \times 19 \cdot 91$

Formula of the chloride of the element : MCl_x

∴   Formula weight $= 19 \cdot 91x + 35 \cdot 5x = 55 \cdot 41x$

∴ $55 \cdot 41x = 111$

$$\therefore \quad x = \frac{111}{55 \cdot 41} = 2 \text{ (nearest whole number)}$$

∴   Exact at. wt. $= 2 \times 19 \cdot 91 = 39 \cdot 82$.

Questions

Long Answer Type :

1. What do you understand by the valency of elements ? How is it measured ? Arrange the following elements in the order of increasing valency :

Carbon, Nitrogen, Chlorine, Calcium, Mercury.

2. Describe how would you determine the equivalent weight of Zinc ?

3. What do you mean by the equivalent weight of a metal ? Describe briefly the method adopted for the determination of equivalent weight of a metal which does not liberate Hydrogen from an acid.

4. How is the equivalent weight of Magnesium determined in the laboratory ?

5. Explain equivalent weight, atomic weight and valency of an element. Show that,

At. Wt. = Eq. Wt. × Valency.   (Mith. U. 1974 A)

6. State Dulong and Petit's Law and indicate its utility in the determination of the atomic weight of an element. What are the defects of this law ?

(R. U. 1977A; M. U. '77 A)

7. Give the method of calculation for the determination of the equivalent weight of a metal by hydrogen displacement method.

8. Explain clearly what do you understand by the "variable valency" of an element.

Short Answer Type :

1. Define equivalent weight of an element.
2. What do you mean by atomic weight ?
3. What do you understand by variable equivalent weight ?
4. What is gm-equivalent ?
5. Give the names of four methods for the determination of atomic weight of an element.
6. Prove that, **at. wt. = equivalent wt. × valency.**
7. Explain the terms (i) Equivalent weight and (ii) Gram-equivalent.
8. Distinguish between equivalent weight of hydrogen and gm-equivalent of hydrogen.

Objective Questions :

(A) *Put T for true statements and F for false statements in the given Answer boxes* :

1. The maximum weight of Ag which can be displaced from $AgNO_3$ solution by 0·1 gm equivalent of Mg is 2·2 g.   □

2. The product of atomic weight and specific heat of solid elements is approximately 6·4   □

3. The valency of an element is determined by the number of Oxygen atoms which combine with one atom of the element.   □

4. 20 g of a certain metal displaces 2·0 g of H_2 at N.T.P. The equivalent weight of the metal is 10.   □

5. In cuprous oxide (Cu_2O) and cupric oxide (CuO) both, the valency of copper is the same.   □

[**Ans.** : 1. F; 2. T; 3. F; 4. T; 5. F.]

(B) *Fill in the blanks with suitable word given in the brackets* :

1. One gm-equivalent of a metal displaces..............litre of Hydrogen at N.T.P. from an acid.   (5·6) (11·2)

2. The equivalent weight of the metal, 1·2 parts by weight of which combine with 0·8 part by weight of oxygen is................   (24); (12)

3. The oxide of an element contains 20% oxygen. The equivalent weight of the metal is................   (32) (16)

4. The equivalent weight of an element M is 9 and its oxide is M_2O_3. The atomic weight of M is................   (27) (18)

[**Ans.** : 1. 11·2; 2. 12; 3. 32; 4. 27.]

(C) *To each question below four answers are given but only one of them is correct. Select the correct answer.*

1. A_1 g of an element gave A_2 g of its oxide. The equivalent wt. of the element is :

(a) $\dfrac{A_2 - A_1}{A_1} \times 8$, (b) $\dfrac{A_1}{(A_2 - A_1)} \times 8$, (c) $\dfrac{A_2 - A_1}{8} \times 8$

(d) $\dfrac{A_2 - A_1}{A_2} \times 8$.

2. 1 g of Hydrogen combines with 80g of Bromine. 1 g of Calcium combines with 4g of Bromine. The eq. wt. of Calcium is

(a) 4,   (b) 40,   (c) 20,   (d) 80.

3. An element forms three compounds having molecular weights 82, 64 and 57. The weights of element present in one gm-mole of these compounds are 36, 24 and 48 respectively. The atomic weight of the element is

(a) 24,   (b) 12,   (c) 48,   (d) none of these.

4. 1g of a metal required 50 ml of 0·5N HCl to dissolve it. The equivalent weight of the metal is

(a) 20,   (b) 25,   (c) 40,   (d) 50.

5. A metal oxide is reduced by heating in a stream of Hydrogen. It is found that after complete reduction, 3·15g of the oxide have yielded 1·05 g of the metal $(O=16)$.

a. We may deduce that—

(i) the at. wt. of the metal is 8, (ii) the atomic weight of the metal is 4, (iii) the eq. wt. of the metal is 4, (iv) the eq. wt. of the metal is 8.

b. the wt. of water produced will be—

(i) 2·362 g,   (ii) 18·3 g,   (iii) 4·721 g,   (iv) 2·442 g.

6. In a metallic oxide (MO) if 1·6g of Oxygen is mixed with 6·32 g of metal the equivalent weight of metal M is

(i) 31·6,   (ii) 63,   (iii) 94·5,   (iv) 126 4.

7. Which of the following is the correct relation

(i) Molecular weight $= \dfrac{\text{Atomic weight}}{\text{Valency}}$.

(ii) Atomic weight $=$ Eq. wt. $\times$ Valency.

(iii) Eq. wt. $=$ Atomic weight $\times$ Valency.

(iv) None of these.

8. The equivalent weight of sulphuric acid is

(i) 98,   (ii) 49,   (iii) 9·8,   (iv) 4·9.

9. The molecular weight of $NaOH$ is 40. Its equivalent weight will be

(i) 40,   (ii) 20,   (iii) 80,   (iv) 60.

10. The atomic weight of an element is 12 and its equivalent weight is 3. The valency of the element is

(i) 3,   (ii) 12,   (iii) 4,   (iv) 36.

11. 8 g of copper is dissolved in nitric acid. The resulting nitrate on being heated gave 10 g of oxide. The equivalent weight of copper is

(i) 64,   (ii) 16,   (iii) 48,   (iv) 32.

12. When steam is passed over red-hot iron, H_2 is obtained according to the equation,

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$
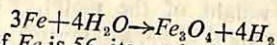
If the atomic weight of Fe is 56, its equivalent weight will be

(i) 42,   (ii) 21,   (iii) 63,   (iv) 84.

13. The weight of a metal after burning in oxygen increases by 24%. The equivalent weight of the metal is

(i) 25,   (ii) 24,   (iii) 76,   (iv) 33·3.

14. The oxide of a metal has the formula M_2O_3. If the equivalent weight of the metal is 9, the atomic weight of the metal will be

(i) 9,   (ii) 27,   (iii) 18,   (iv) none of these.

15. The specific heat of an element is 0·16. The atomic weight of the element is

(i) 20,   (ii) 30,   (iii) 64,   (iv) 40.   **(MDAT 1979)**

16. If the molecular weight of a dibasic acid is M, its equivalent weight is

    (i) 2 M,   (ii) $M/_3$,   (iii) $M/_2$,   (iv) $\sqrt{M}$.   **(MDAT 1980)**

17. The vapour density of the chloride of a metal is 66. The oxide of the metal contains 53% of the metal. The valency of the metal is

    (i) 1,   (ii) 2,   (iii) 3,   (iv) 4,   (v) 5.

18. The chloride of a metal contains 79·77% chlorine. The specific heat of the metal is 0·237. The atomic weight of the metal is

    (i) 9,   (ii) 18,   (iii) 27,   (iv) 36,   (v) 45.

19. 1·4 g of a divalent metal displaces all the hydrogen from 2·45 g of sulphuric acid. The atomic weight of the metal is

    (i) 16,   (ii) 14,   (iii) 56,   (iv) 70.

20. The molecular formula of a metal chloride is MCl and its molecular weight is 74·5. The equivalent weight of the metal is

    (i) 74·5,   (ii) 39,   (iii) 110,   (iv) 88.

[Ans. **1.** b; **2.** c; **3.** a; **4.** c; **5a.** (iii); **5b.** (i); **6.** (i); **7.** (ii); **8.** (ii); **9.** (i); **10.** (iii); **11.** (iv); **12.** (ii); **13** (i); **14.** (ii); **15.** (iv); **16.** (iii); **17.** (iv); **18.** (iii); **19.** (ii); **20.** (ii)].

Numerical Problems :

1. 2·943 g of a metal was treated with excess of sulphuric acid. The volume of Hydrogen collected over water at 15°C and 752·5 mm. pressure was found to be 1083·6 ml. Calculate the equivalent weight of the metal. (Aqueous tension at 15°C = 12·6 mm, and weight of 1 ml of Hydrogen at N.T.P. = 0·00009 g).
       (Ans. 32·97)

2. 1·62 g of Zinc was converted into nitrate by dissolving in nitric acid. The nitrate, on strong heating, left 2·02 g of the oxide. Find the equivalent weight of Zinc.   (Ans. 32·4)

3. 1 g of a metal when treated with dil. H_2SO_4 gave 922 ml of Hydrogen at N. T. P. Find the equivalent weight of the metal.   (Ans. 12·14)

4. 3·2203 g of carbon in the form of diamond yields on combustion 11·8057 g of carbon dioxide. Calculate the equivalent weight of Carbon.   (Ans. 3)

5. 5 g of a metal liberate 0·0346 g of Hydrogen from HCl, and the same weight of the metal yields 6·35 g of its oxide. Calculate the equivalent weight of the metal.   (Ans. : 144·5; 29·6)

6. 0·344 g of Tin combines with Oxygen to give 0·4365 g of SnO_2. What is the Eq. wt. of tin ?   (Ans. 29·7)

7. 100 g of Mg combine with 65·6 g of Oxygen. 8 g of Oxygen combine with 1 g of Hydrogen. Find the equivalent weight of Magnesium.   (Ans. 12·19)

8. The chloride of a metal M contains 47·25% of the metal. 1 g of the metal would be displaced from a compound by 0·88 g of another metal N. Find the equivalent weights of M and N.

[**Hint :**   Chlorine = 100 − 47·25 = 52·75%

$$\therefore \quad \text{Eq. wt. of } M = \frac{47·25}{52·75} \times 35·5 = 31·79$$

Again,   1 g of M displaces   0·88 g of N,

$$\therefore \quad 31·79 \text{ g} \quad ,, \quad \frac{0·88 \times 31·79}{1} \text{ g of } N$$

$$= 27·97 = \text{Eq. wt. of } N]$$

9. When Hydrogen is passed over excess of copper oxide, the oxide loses 59·789 g in wt., and 67·28 g of water are formed. Calculate the equivalent weight of Oxygen.   (Ans. 7·98)

10. 5·6 g of $ZnCl_2$ require 8·866 g of silver for completely precipitating the chlorine as $AgCl$. Assuming the equivalent weights of silver and chlorine to be 107·88 and 35·46 respectively. Calculate the equivalent weight of Zinc.

(Ans. 32·68)

11. The chloride of an element contains 38·11% of chlorine. Find the equivalent weight of the element $(Cl = 35·46)$.

(Ans. 57·58)

12. The same current was passed through solutions of $Pb(NO_3)_2$ and $ZnSO_4$. It was found that the weights of Pb and Zn deposited were 6·903 g and 2·18 g. Calculate the equivalent weight of Pb, that of Zn being 32·7. (Ans. 103·54)

13. Calculate the equivalent weight of a metal, 0.3070 g of which when placed n solution of $AgNO_3$, displaced 1·775 g of silver. (Equivalent wt. of $Ag = 108$)

(Ans. 18·66)

14. A metal forms two chlorides containing 34·4% and 44% of the metal. Deduce the equivalent weights of the metal.

(Ans. 18·62 and 27·80)

15. 1·49 g of KCl gave 2·87 g of $AgCl$ on treatment with a solution of $AgNO_3$. Calculate the equivalent weight of Potassium, those of chlorine and silver being 35·5 and 108 respectively.

(Ans. 39)

16. 1·520 g of a hydroxide of a metal gave on heating 0·5 g of its oxide. Calculate the equivalent weight of the metal.

(Ans. 12·0)

17. The chloride of a metal contains 47·22% of the metal. Its specific heat is 0·094. What is its exact atomic weight ?

18. The specific heat of an element is 0·198. What is its probable atomic weight ?

(Ans. 32·32)

19. 0·1166 g of the chloride of a metal yields 0·304 g of $AgCl$ on treatment with a solution of silver nitrate. The specific heat of the metal is 0·15. Calculate the equivalent wt. and atomic wt. of the metal.

(M. U. 1974A)

20. The chloride of a metal contains 65·61% of chlorine. The specific heat of the metal is 0·11. Find the Eq. wt., At. wt. and Valency of the metal.

(Ans. 18·61, 55·83, 3)

21. On heating 4·215 g of the carbonate of a metal in a hard glass tube 1336 ml of CO_2 is evolved at 27°C and 700 mm pressure. What is the equivalent weight of the metal ?

(I.I.T. 1979) [Ans. 12.15]

22. Two oxides of a metal contain 36·8% and 30·38% of Oxygen. The specific heat of the metal is 0·117. Calculate the accurate atomic weight of the metal and assign the formulae to its two oxides.

(Ans. 54·96; MO_2, M_2O_3)

23. The sulphate of a metal contains 20·9% of the metal and is isomorphous with $ZnSO_4.7 H_2O$. What is the atomic weight of the metal ? $(Zn = 65)$

(Ans. 58·65)

24. The percentage of Carbon in four of its compounds are 92·2, 62·0, 40·0 and 15·8 respectively. The vapour densities of the compounds are 39, 29, 30 and 38 respectively. Deduce the atomic weight of Carbon.

(Ans. 12)

□ □ □

CHEMICAL CALCULATIONS

Empirical or Simple Formula—The empirical formula of a compound is the simplest formula which shows the relative number of atoms of each element present in a molecule of the compound.

It, however, does not represent the actual number of atoms of elements in a molecule of the compound.

It is deduced from the percentage composition of the compound.

Example : (i) The molecular formula of acetic acid is $C_2H_4O_2$. It contains 2 atoms of C, 4 atoms of H and 2 atoms of O. The ratio of C, H and O atoms is $2:4:2$. But the simplest ratio will be $1:2:1$. Hence, the empirical formula of acetic acid will be CH_2O.

(ii) The molecular formula of benzene is C_6H_6. The ratio of C and H atoms in a molecule of benzene is thus $6:6$. The simplest ratio will be $1:1$. Hence, the empirical formula of benzene is CH.

(iii) In a molecule of acetylene (C_2H_2) the ratio of C and H atoms is $2:2$. The simplest ratio is $1:1$. Hence, the empirical formula of acetylene is CH.

It is, thus, seen that benzene and acetylene have the same empirical formula (CH), but their molecular formulae are different.

Empirical formula from percentage composition :

Rule : (i) Divide the percentage amount of each element present in the compound by the atomic weight of the element concerned. This gives the ratio of atoms.

(ii) In order to express this ratio as whole numbers each is divided by the smallest number obtained.

(iii) The quotients are then multiplied by a common number, if need be, to make them all integrals.

Illustrations

1. An organic compound is found to have the following percentage composition :

$$C = 12 \cdot 76\%, \quad H = 2 \cdot 13\% \text{ and } Br = 85 \cdot 11\%$$

Find out the empirical formula of the compound.

Solution :

Element	% Composition	Atomic weight	% Composition / At. wt.	Ratio of atoms	Dividing each by the smallest number	Ratio in whole number
C	12·76	12	$\dfrac{12·76}{12}$	1·06	1	1
H	2·13	1	$\dfrac{2·13}{1}$	2·13	2·00	2
Br	85·11	80	$\dfrac{86·11}{80}$	1·07	1·00	1

Empirical formula of the compound is CH_2Br.

2. An organic compound containing C, H and O was subjected to combustion. 1·367 g of the compound gave 3·002 g CO_2 and 1·640 g H_2O. Find out the empirical formula of the compound.

(I. I. T. 1975)

Solution : % of $C = \dfrac{3·002 \times 12 \times 100}{44 \times 1·367} = 60\%$

% of $H = \dfrac{1·640 \times 2 \times 100}{18 \times 1·367} = 13·3\%$

$\therefore$ % of $O = 100 - (60 + 13·3) = 26·7\%$

Element	% Composition	Atomic weight	% Composition / At. wt.	Ratio of atoms	Dividing each by the smallest number	Ratio in whole number
C	60	12	$\dfrac{60}{12}$	5	3·01	3
H	13·3	1	$\dfrac{13·3}{1}$	13·3	8·01	8
O	26·7	16	$\dfrac{26·7}{16}$	1·66	1	1

$\therefore$ Empirical formula of the compound is C_3H_8O.

Molecular Formula : The molecular formula of a compound is the symbolic representation of a molecule of the compound, and shows the actual number of atoms of each element present in one molecule of the compound.

Example : (i) One molecule of water contains two H atoms and one O atom. Hence, the molecular formula of water is H_2O.

(ii) One molecule of calcium chloride contains one atom of Ca and two atoms of Cl. Hence, the molecular formula of calcium chloride is $CaCl_2$.

(iii) A molecule of benzene contains six atoms of C and six atoms of H. Hence, the molecular formula of benzene is C_6H_6.

Distinctions between the Empirical formula and the Molecular formula :

(i) The empirical formula shows the simplest ratio of atoms of each element present in a molecule of the compound, but the molecular formula shows the exact number of atoms of each element present in a molecule.

The empirical formulae of both benzene and acetylene is CH, but their molecular formulae are C_6H_6 and C_2H_2 respectively.

(ii) In order to establish the molecular formula of a substance, its molecular weight must be known. This is, however, not the case with the empirical formula.

(iii) The molecular formula is always either identical with or is a simple multiple of the empirical formula. Thus,

Molecular formula = (Empirical formula) $\times n$

where, $n = 1, 2, 3, 4, \ldots$ etc.

$$\therefore \quad n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}.$$

Illustrations

3. A compound on being analysed, gives the following results :

$$C = 92 \cdot 4\%, \text{ and } H = 7 \cdot 6\%$$

The molecular weight of the compound is 78. Find its molecular formula.

Solution :

Element	% Composition	Atomic weight	$\frac{\% \text{ Composition}}{\text{At. wt.}}$	Ratio of atoms	Dividing each by the smallest number	Ratio in whole number
C	92·4	12	$\frac{92 \cdot 4}{12}$	7·7	1·00	1
H	7·6	1	$\frac{7 \cdot 6}{1}$	7·6	1	1

$\therefore$ Empirical formula : CH

Let the molecular formula be $(CH)_n$.

$$\therefore \quad n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

$$= \frac{78}{13} = 6$$

$\therefore$ Molecular formula is C_6H_6.

4. The empirical formula of a compound is C_2H_4O. If the vapour density of the compound is 44, find out its molecular formula.

Solution : Vapour density $= 44$

$\therefore$ Molecular weight $= 2 \times 44 = 88$

Empirical formula is C_2H_4O.

$\therefore$ Empirical formula weight $= 2 \times 12 + 4 \times 1 + 16 = 44$

Let the molecular formula be $(C_2H_4O)_n$.

$$\therefore \quad n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

$$= \frac{88}{44} = 2$$

$\therefore$ Molecular formula is $C_4H_8O_2$.

5. 0 15 g of a liquid A on evaporation occupied 62·4 ml at 27°C and 750 mm pressure. A contains 40% C, 6·67% H and the rest oxygen. From these data, find out the molecular formula of A.

(M. U. 1963A)

Solution : Let the volume of vapour at N.T.P. be V ml. According to the combined gas law,

$$\frac{760 \times V}{273} = \frac{750 \times 62 \cdot 4}{(273 + 27)}$$

$$\therefore \qquad V = \frac{273 \times 750 \times 62 \cdot 4}{760 \times (273 + 27)} = 56 \cdot 0 \text{ ml}$$

Now, according to Avogadro's law, the mass of 22·4 litres of a gas at N.T.P. is equal to its gram molecular weight. Thus,

$\because$ 56·0 ml gas at N. T. P. weighs 0·15 g,

$\therefore$ 22·4 × 1000 ml ,,   ,,   ,, $\dfrac{0 \cdot 15 \times 22400}{56}$ g $= 60$ g.

i.e., Molecular weight $= 60$.

% amount of oxygen in $A = 100 - (40 + 6 \cdot 67)$

$$= 53 \cdot 33\%,$$

Element	% Composition	Atomic weight	% Composition / At. wt.	Ratio of atoms	Dividing each by the smallest number	Ratio in whole number
C	40	12	$\dfrac{40}{12}$	3·33	1	1
H	6·67	1	$\dfrac{6·67}{1}$	6·67	2	2
O	53·33	16	$\dfrac{53·33}{16}$	3·33	1	1

∴ Empirical formula is CH_2O

Empirical formula weight $= 12 + 2 + 16 = 30$

Let the molecular formula be $(CH_2O)_n$.

∴ $\quad n = \dfrac{\text{Molecular weight}}{\text{Empirical formula weight}} = \dfrac{60}{30} = 2$

∴ Molecular formula is $C_2H_4O_2$.

6. Two oxides of a metal contain 27·6% and 30% oxygen respectively. If the formula of one oxide is M_3O_4, what is the formula of the other oxide ?
(M. U. 1970S; '73S)

Solution : Let the two oxides be X and Y. The composition of these oxides will then be as :

	Oxygen	Metal
X	27·6%	$100 - 27·6 = 72·4$
Y	30%	$100 - 30 = 70\%$

Let the atomic weight of the metal be x.

In X, $\quad \dfrac{\text{number of } O \text{ atoms}}{\text{number of metal atoms}} = \dfrac{4}{3}$

Again, number of O atoms in $X = \dfrac{27·6}{16}$

And, number of metal atoms in $X = \dfrac{72·4}{x}$;

∴ $\quad \dfrac{27·6}{16} \Big/ \dfrac{72·4}{x} = \dfrac{4}{3}$

∴ $\quad x = 55·74$

Now, **Oxide Y** :

Element	% Composition	Atomic weight	$\dfrac{\text{\% Composition}}{\text{At. wt.}}$	Ratio of atoms	Dividing each by the smallest number	Ratio in whole number
M	70	55·75	$\dfrac{70}{55·74}$	1·26	1	2
O	30	16	$\dfrac{30}{16}$	1·88	1·5	3

∴ Formula of Y will be M_2O_3.

7. A certain compound containing C and O only has an approximate molecular weight of 290. On analysis it was found to contain 50% of each element. Find the molecular formula of the compound.

(I. I. T. 1970)

Solution :

Element	% Composition	Atomic weight	$\dfrac{\text{\% Composition}}{\text{At. wt.}}$	Ratio of atoms	Dividing each by the smallest number	Ratio in whole number
C	50	12	$\dfrac{50}{12}$	4·166	1·33	4
O	50	16	$\dfrac{50}{16}$	3·125	1	3

∴ Empirical formula is C_4O_3
Empirical formula weight $= 48 + 48 = 96$
Let the molecular formula be $(C_4O_3)_n$.

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{290}{96} = 3$$

∴ Molecular formula will be $C_{12}O_9$.

8. A sample of a volatile compound, 0·220 g containing carbon, hydrogen and chlorine only, yielded on combustion in oxygen 0·195 g of CO_2 and 0·0804 g of H_2O. 0·120 g of the compound occupied a volume of 37·24 ml at 105°C, 768 mm Hg pressure. Calculate the molecular formula of the compound

(I. I. T. 1978)

Solution : Weight of volatile compound $= 0·220$ g
Weight of Carbon from $CO_2 = \frac{12}{44} \times 0·195 = 0·0532$ g.
Weight of Hydrogen from $H_2O = \frac{2}{18} \times 0·0804 = 0·00893$ g.

Weight of Chlorine by difference $= 0.22 - (0.0532 + 0.00893)$
$$= 0.15787g$$

Atomic ratio : $\quad C : H : Cl = \dfrac{0.0532}{12} : \dfrac{0.00893}{1} : \dfrac{0.15787}{35.5}$

$$= 0.0044 : \quad 0.0089 \quad : \quad 0.0044$$
$$= 1 : 2 : 1$$

$\therefore$ Empirical formula of the compound : CH_2Cl

Calculation of Molecular Weight :

Volume of 0.120 g of compound at N. T. P.

$$= \frac{37.24 \times 768 \times 273}{760 \times 378} = 27.18 \text{ ml.}$$

$\therefore$ Molecular weight $=$ Weight of 22.4 litre at N. T. P.
Weight of 27.18 ml at N. T. P. $= 0.12$ g

$\therefore$ Weight of $22,400$ ml at N. T. P. $= \dfrac{0.12 \times 22,400}{27.18}$

$$= 98.9 \text{ g}$$
$\therefore$ Molecular weight of compound $= 98.9$.

Calculation of Molecular formula :

Let the molecular formula of the compound be $(CH_2Cl)_n$

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}}$$

$$= \frac{98.9}{49.5} = 1.99 = 2$$

$\therefore$ Molecular formula : $(CH_2Cl)_2$ or $C_2H_4Cl_2$

CALCULATIONS BASED ON CHEMICAL EQUATIONS

(A) Calculations involving weight and weight :

When the equation representing a chemical reaction is known, we can easily calculate either the amount of the reactants required to produce a given quantity of the product, or the amount of the product formed from the given amounts of the reactants.
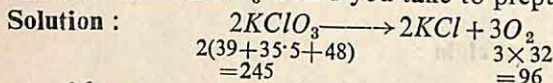
Solved Problems

1. Find the weight of quicklime (CaO) produced by strongly heating 10 g of limestone. $(Ca = 40, C = 12, O = 16)$

Solution :

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$(40+12+48) \quad (40+16)$$
$$=100 \quad\quad =56$$
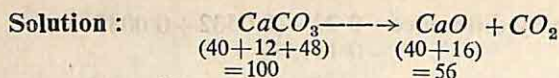
∵ 100 g of limestone gives 56g of quicklime,

∴ 10 g ,, ,, ,, $\dfrac{56 \times 10}{100}$ g ,,

$$= 5\cdot6 \text{ g} \qquad ,,$$

2. How much $KClO_3$ would you take to prepare 5 g of oxygen ?

Solution :

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$
$$2(39+35\cdot5+48) \quad\quad 3\times32$$
$$=245 \quad\quad =96$$

∵ 96 g oxygen is obtained from 245 g $KClO_3$,

∴ 5 g ,, ,, $\dfrac{245 \times 5}{96}$ g ;,

$$= 12\cdot76 \text{ g} \qquad ,,$$

3. 2·4 g of magnesium is treated with 14 g of hydrochloric acid. Find the weight of hydrogen obtained.

Solution :

$$\underset{24}{Mg} + \underset{(2\times36\cdot5)}{2HCl} \longrightarrow MgCl_2 + \underset{2}{H_2}$$
$$=73$$
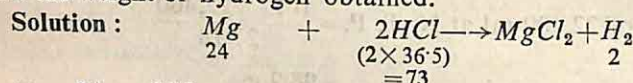
∵ 24 g of Mg reacts with 73g of HCl,

∴ 2·4 g ,, ,, $\dfrac{73 \times 2\cdot4}{24}$ g $= 7\cdot3$ g of HCl

The HCl being in excess, we shall use the weight of Mg.
Now, 24 g of Mg gives 2 g of H_2,

∴ 2·4 g ,, ,, $\dfrac{2 \times 2\cdot4}{24}$ g ,, $= 0\cdot2$ g of H_2.

4. Calculate the minimum weight of iron required to produce 40 g of hydrogen.

(A)

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$
$$56 \qquad\qquad\qquad 2$$

(B)

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$
$$(3\times56) \qquad\qquad (4\times2)$$
$$=168 \qquad\qquad =8$$
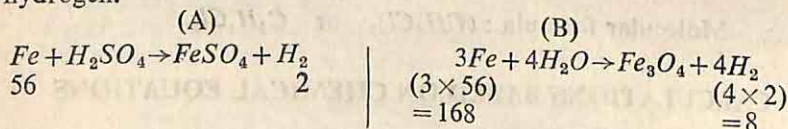
In process (A) 2 gm of H_2 is obtained from 56 g of Fe. Hence,

40g of H_2 would be obtained from $\dfrac{56 \times 40}{2} = 1120$ g of Fe.

In process (B) 8g of H_2 is obtained from 168 g of Fe. Hence, 40 g

of H_2 would be obtained from $\dfrac{168 \times 40}{8}$ g of Fe, i.e., 840 g of Fe.

Thus, in process (B) less iron is required.
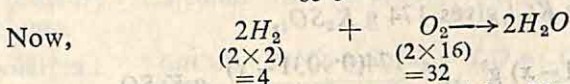
∴ Minimum weight of iron = 840 g.

5. Calculate the weight of potassium chlorate which when strongly heated gives as much oxygen as is required to react completely with hydrogen obtained by treating 6·5 g zinc with dilute sulphuric acid. ($K = 39$, $Cl = 35·5$, $O = 16$, $Zn = 65·5$) (R. U. 1974S)
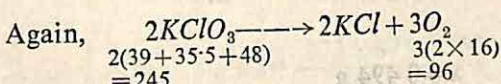
Solution : $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

$\quad\quad\quad 65·5 \quad\quad\quad\quad\quad\quad\quad\quad 2$
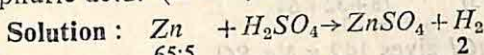
$\because$ 65·5 g of Zn gives 2 g of H_2,

$\therefore$ 6·5 g „   „ $\dfrac{2 \times 6·5}{65·5}$ g „   = 0·195 g of H_2.

Now, $2H_2 + O_2 \rightarrow 2H_2O$

$\quad\quad (2\times2) \quad\quad (2\times16)$
$\quad\quad =4 \quad\quad\quad =32$

$\because$ 4 g of H_2 reacts completely with 32g of O_2,

$\therefore$ 0·195 g „   „   „ $\dfrac{32 \times 0·195}{4}$ g „

$\quad\quad\quad\quad\quad\quad\quad\quad = 1·560$ g   „

Again, $2KClO_3 \longrightarrow 2KCl + 3O_2$

$\quad 2(39+35·5+48) \quad\quad 3(2\times16)$
$\quad =245 \quad\quad\quad\quad\quad =96$

$\because$ 96 g of O_2 is obtained from 245 g of $KClO_3$,

$\therefore$ 1·560 g „   „   „ $\dfrac{245 \times 1·560}{96}$ g „

$\quad\quad\quad\quad\quad\quad\quad = 3·98$ g $KClO_3$.

6. What weight of pyrolusite containing 60% MnO_2 would be required to liberate all the iodine from 100 g of potassium iodide ? ($K = 39$, $Mn = 55$, $I = 127$)

Solution : $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$

$\quad\quad\quad\quad 2KI + Cl_2 = 2KCl + I_2$

Thus, $MnO_2 \equiv Cl_2 \equiv 2KI$

$\quad\quad 55+32 \quad\quad\quad 2(39+127)$
$\quad\quad =87 \quad\quad\quad\quad =332$
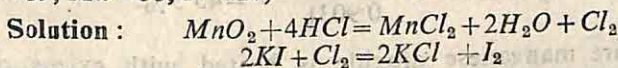
$\because$ 332 g of KI would require 87 g of MnO_2,

$\therefore$ 100 g „   „   „ $\dfrac{87 \times 100}{332}$ g „

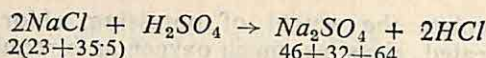$\quad\quad\quad\quad\quad\quad\quad = 26·20$ g   „

$\therefore$ Wt. of pyrolusite $= \dfrac{26·20 \times 100}{60}$ g $= 43·66$ g.

7. 0·9031 g of a mixture of $NaCl$ and KCl was heated with conc. H_2SO_4. The resulting mixture of sulphates weighs 1·0784 g. Find the composition of the mixture ($Cl = 35·5$, $K = 39$).

Solution : Let x be the weight of $NaCl$.

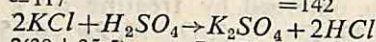$\therefore$ Weight of $KCl = (0·9031 - x)$ g.

Now

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$
$$\begin{matrix} 2(23+35.5) \\ =117 \end{matrix} \qquad \begin{matrix} 46+32+64 \\ =142 \end{matrix}$$

$$2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2HCl$$
$$\begin{matrix} 2(39+35.5) \\ =149 \end{matrix} \qquad \begin{matrix} 78+32+64 \\ =174 \end{matrix}$$

$\because$ 117 g $NaCl$ gives 142 g Na_2SO_4,

$\therefore$ x g   ,,   ,, $\dfrac{x \times 142}{117}$ g ,,

Again, $\because$ 149 g KCl gives 174 g K_2SO_4,

$\therefore$ $(0.9031-x)$ g   ,, $\dfrac{174(0.9031-x)}{149}$ g K_2SO_4.

$\because$ Weight of sulphates $= 1.0784$ g,

$\therefore$ $\dfrac{x \times 142}{117} + \dfrac{174(0.9031-x)}{149} = 1.0784$.

Solving, we get,

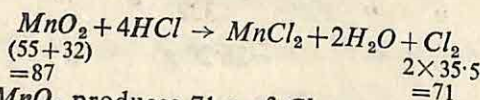$$x = 0.494 \text{ g}$$

i.e.,   weight of $NaCl = 0.494$ g

$\therefore$ weight of $KCl = (0.9031-0.494)$ g
$$= 0.4091 \text{ g}.$$

Hence,   % of $NaCl = \dfrac{0.494 \times 100}{0.9031} = 54.7\%$

$$\% \text{ of } KCl = \dfrac{0.4091 \times 100}{0.9031} = 45.3\%.$$

8. 16 g of pure manganese dioxide is heated with excess of conc. HCl and the gas evolved in the reaction is passed through potassium iodide solution. Find out the weight of iodine liberated.
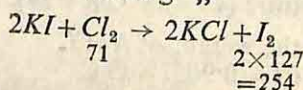$$(Mn=55, \ Cl=35.5, \ K=39)$$

Solution : The reaction between MnO_2 and HCl is represented by the equation,

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$
$$\begin{matrix} (55+32) \\ =87 \end{matrix} \qquad\qquad\qquad \begin{matrix} 2\times35.5 \\ =71 \end{matrix}$$

$\because$ 87 g MnO_2 produces 71 g of Cl_2,

$\therefore$ 16 g   ,,   ,, $\dfrac{71 \times 16}{87}$ g ,,

$$= 13.06 \text{ g ,,}$$

Now, $2KI + Cl_2 \rightarrow 2KCl + I_2$
$$\begin{matrix} 71 \qquad\qquad\qquad 2\times127 \\ =254 \end{matrix}$$

$\therefore$ 71 g of Cl_2 liberates 254 g of I_2,

$\therefore$ 13·06 g   ,,   ,, $\dfrac{254 \times 13·06}{71}$ g of I_2

$$= 46·71 \text{ g.}$$

9. A sample of calcium carbonate contains impurities which do not react with a mineral acid. When 2·0 g of the sample reacted with a mineral acid, 875 ml of CO_2 was obtained at 27°C and 750 mm pressure. Calculate the percentage purity of the sample of carbonate. **(I. I. T. Adm. Test, 1964)**

Solution : $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
100 g   22·4 litre
                                        at N.T.P.
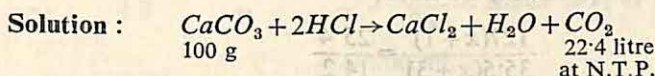
Let the volume of CO_2 evolved at N.T.P. be V_0 ml. Then

$$\frac{760 \times V_0}{273} = \frac{750 \times 875}{(273 + 27)} = \frac{750 \times 875}{300}$$

or $V_0 = \dfrac{273 \times 875 \times 750}{300 \times 760}$ ml = 341·25 ml.

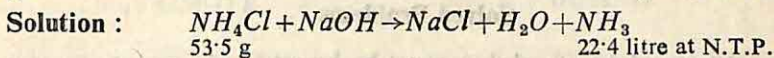Now, 22400 ml CO_2 at N.T.P. is obtained from 100 g $CaCO_3$,

$\therefore$ 341·25   ,,   ,,   ,,   ,, $\dfrac{100 \times 341·25}{22400}$ g $CaCO_3$

$$= 1·52 \text{ g } CaCO_3$$

$\therefore$ Percentage purity of Calcium carbonate $= \dfrac{1·52}{2·0} \times 100$

$$= 76\%.$$

10. Calculate the weight of NH_4Cl required to give 10 litres of NH_3 measured at N.T.P. **(Bhag. U. 1974)**

Solution : $NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$
53·5 g   22·4 litre at N.T.P.

$\therefore$ 22·4 litres of NH is obtained from 53·5 g NH_4Cl,

$\therefore$ 10   ,,   ,,   ,,   ,, $\dfrac{53·5 \times 10}{22·4}$ g NH_4Cl

$$= 23·9 \text{ g.}$$

11. 25·4 g of iodine and 14·2 g of chlorine are made to react completely to give a mixture of ICl and ICl_3. Calculate the ratio of the moles of ICl and ICl_3 formed. **(I. I. T. Adm. Test 1970)**

Solution : Let the ratio of the moles of ICl and ICl_3 be $x : 1$.

Moles of $ICl = x$ $(ICl_3 \equiv 1)$
Gm-atoms of $I = x$ Moles of $ICl_3 = 1$ ($\because$ $ICl_3 \equiv 1$)
                             $\therefore$ Gm-atom of $I = 1$.

$\therefore$ Total moles of $I_2 = \dfrac{x+1}{2}$

$\therefore$ Wt. of $I_2 = 127(x+1)$.

Now,   moles of $ICl = x$ ($\because ICl \equiv Cl$)

$\therefore$ gm- atoms of $Cl = x$

          Moles of $ICl_3 = 1$

$\therefore$ Atoms of $Cl = 1 \times 3 = 3$ ($ICl_3 \equiv 3Cl$)

$\therefore$ Total number of gm. atoms of $Cl = x + 3$.

$\therefore$ Wt. of $Cl = 35 \cdot 5 (x+3)$.

Now, from the problem, we have,

$$\frac{127(x+1)}{35 \cdot 5(x+3)} = \frac{25 \cdot 4}{14 \cdot 2}$$

$\therefore$ $x = 1$. $\therefore$ Ratio $= 1 : 1$.

(B) Calculations involving Weight and Volume :

In such calculations the following points are to be noted :

(i) An equation represents a chemical reaction occurring at N. T. P.

(ii) The gram molecular volume of a gas at N.T.P. is $22 \cdot 4$ litre.

$2H_2$	$+$	O_2	$=$	$2H_2O$ (steam)
$2 \times 22 \cdot 4$ litres		$22 \cdot 4$ litres		$2 \times 22 \cdot 4$ litres
(N.T.P.)		(N.T.P.)		(N.T.P.)
or, 2 volumes		or, 1 volume		or 2 volumes
or, 4 g		32 g		36 g

(iii) Such volume calculations do not apply to solids or liquids. It applies only to gases or vapours.

(iv) One litre of H_2 at N.T.P. weighs $0 \cdot 09$ g.

(v) Molecular weight of a gas $= 2 \times$ its vapour density.

Solved Problems

1. What weight of sulphur must be burnt in air so as to produce 10 litres of sulphur dioxide at N.T.P. ?

Solution : $S + O_2 = SO_2$
                              32       $22 \cdot 4$ litre at N.T.P.

$\because$ $22 \cdot 4$ litres of SO_2 is obtained from 32 g of S,

$\therefore$ 10 litres   ,,   ,,   ,, $\dfrac{32 \times 10}{22 \cdot 4}$ g of S

                                        $= 14 \cdot 28$ g of S.

2. What weight of sulphuric acid will be required to dissolve completely 3 g of $MgCO_3$? Calculate the volume of CO_2 gas evolved at N.T.P.

Solution : $MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2O + CO_2$
$\underset{=84}{(24+12+48)} \quad \underset{=98}{2+32+64} \qquad\qquad \underset{\text{at N.T.P.}}{\text{22·4 litres}}$

$\therefore$ 84 g of $MgCO_3$ dissolves in 98 g of H_2SO_4,

$\therefore$ 3 g   ,,   ,,   ,, $\dfrac{98 \times 3}{84}$ g   ,,

$= 3\cdot5$ g H_2SO_4.

Again, 84 g of $MgCO_3$ gives 22·4 litres CO_2 at N.T.P.,

$\therefore$ 3 g   ,,   ,, $\dfrac{22\cdot4 \times 3}{84}$ litres CO_2 at N.T.P.

$= 800$ ml.

3. 1 g of an alloy of aluminium and magnesium is treated with excess of hydrochloric acid to form aluminium chloride, magnesium chloride and hydrogen. The hydrogen collected over mercury is found to occupy 899 ml at 760 mm pressure and 0°C. Determine the composition of the alloy. $(Al = 27, Mg = 24)$ (I.I.T Adm. Test 1971)

Solution : Let x g be the weight of Al.

$\therefore$ Wt. of $Mg = (1-x)$ g.

Now, $\underset{\substack{2\times27 \\ =81}}{2Al} + 6HCl \rightarrow 2AlCl_3 + \underset{\substack{3\times22\cdot4 \text{ litres at N.T.P.} \\ =67\cdot2 \text{ litres}}}{3H_2}$

$\underset{24}{Mg} + 2HCl \rightarrow MgCl_2 + \underset{22\cdot4 \text{ litres at N.T.P.}}{H_2}$

$\therefore$ 81 g of Al gives 67·2 litres of H_2 at N.T.P.

$\therefore$ x g   ,,   ,, $\dfrac{67\cdot2 \times x}{81}$ litres H_2 ... (a).

Again, $\therefore$ 24 g of Mg gives 22·4 litres at N.T.P.,

$\therefore$ $(1-x)$ g   ,,   ,, $\dfrac{22\cdot4(1-x)}{24}$ litres H_2 ... (b).

$\therefore$ Total H_2 evolved at N.T.P. $= \left[\dfrac{67\cdot2 \times x}{81} + \dfrac{22\cdot4(1-x)}{24} \right]$

litres.

Volume of $H_2 = 899$ ml $= 0\cdot899$ litre.

$\therefore$ $\dfrac{67\cdot2 \times x}{81} + \dfrac{22\cdot4(1-x)}{24} = 0\cdot899$

By Solvent $x = 0\cdot326$ g

i.e.,   wt. of $Al = 0\cdot326$ g

$\therefore$ wt. of $Mg = 1 - 0\cdot326 = 0\cdot674$ g.

Hence   % of $Al = 32\cdot6\%$

% of $Mg = 67\cdot4\%$.

4. What weight of iodine is liberated from excess of potassium iodide by the action of one litre of chlorine measured at 10°C and 750 mm ?

Solution : Volume of $Cl_2 = 1$ litre   Normal pressure $= 760$ mm
Pressure $= 750$ mm   Normal temp. $= 273$ K
Temp. $= 10°C = 283$ K.

Let the volume of Cl_2 at N.T.P. be V litre. Then,

$$\frac{750 \times 1}{283} = \frac{760 \times V}{273}$$

or

$$V = \frac{750 \times 273}{760 \times 283} \text{ litre}$$

$$= 0\cdot95 \text{ litre.}$$
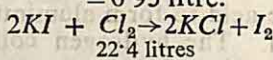
Now, $2KI + Cl_2 \rightarrow 2KCl + I_2$
                22·4 litres 2×127 g

$\because$ 22·4 litres of Cl_2 at N.T.P. gives 2×127 g of I_2,

$\therefore$ 0·95   ,,   ,,   ,, $\dfrac{2 \times 127 \times 0\cdot95}{22\cdot4}$ g of I_2

$$= 10\cdot77 \text{ g of } I_2.$$

5. 1 g of a mixture of dry sodium carbonate and sodium bicarbonate in equal proportions by weight is ignited until there is no more loss in weight. What volume of CO_2 is evolved at N.T.P. ?

Solution :   Wt. of dry $Na_2CO_3 = 0\cdot5$ g
         Wt. of $NaHCO_3 = 0\cdot5$ g.

On ignition Na_2CO_3 does not decompose. Only $NaHCO_3$ undergoes decomposition as shown below :

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
2(23+1+12+48)   22·4 litres
$= 168$ at N.T.P.
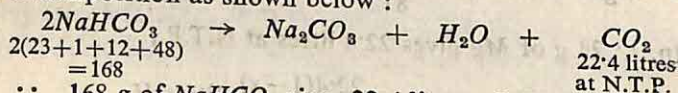
$\because$ 168 g of $NaHCO_3$ gives 22·4 litres of CO_2 at N.T.P.,

$\therefore$ 0·5 g $NaHCO_3$ gives $\dfrac{22\cdot4 \times 0\cdot5}{168}$ litre at N.T.P.

$$= 0\cdot066 \text{ litre at N.T.P.}$$
$$= 66 \text{ ml.}$$

6. 8·5 g of sodium nitrate is heated with sodium hydroxide solution and zinc. Find the weight and volume of ammonia gas obtained at 20°C and 750 mm pressure ($Na = 23$, $N = 14$, $O = 16$).

Solution : Nascent hydrogen is obtained by the reaction between $NaOH$ and Zn. This hydrogen reduces $NaNO_3$ to give NH_3 gas.

$NaNO_3 + 8H \rightarrow NaOH + 2H_2O + NH_3$
23+14+48   22·4 litres.
$= 85$ at N.T.P.
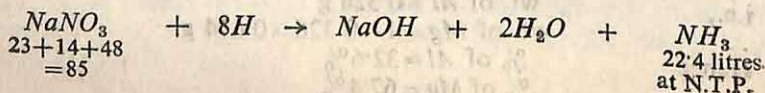
∵   85 g of $NaNO_3$ gives 22·4 litres of NH_3 gas at N.T.P.,

∴   8·5   g   of $NaNO_3$ gives $\dfrac{22·4 \times 8·5}{85}$ litre at N.T.P.

$$= 2·24 \text{ litres at N.T.P.}$$

Let the volume of 2·24 litres NH_3 be V litre at 20°C and 750 mm

$$\therefore \quad \frac{760 \times 2·24}{273} = \frac{750 \times V}{(273+20)}$$

or $V = \dfrac{760 \times 2·24 \times 293}{273 \times 750} = 2·43$ litres.

Again,   ∵   22·4 litres of NH_3 at N.T.P. weigh 17 g,

∴   2·24 litres of NH_3 at N.T.P. weighs $\dfrac{17 \times 2·24}{22·4}$ g $= 1·7$ g.

7.   1 g of a mixture of $CaCO_3$ and $MgCO_3$ gives 240 ml of CO_2 at N.T.P. Calculate the composition of the mixture. **(Bhag. U. 1977 A)**

Solution :   Let the weight of $CaCO_3$ be x g.

∴   Weight of $MgCO_3 = (1-x)$ g.

$$
\begin{array}{ccccc}
CaCO_3 & \rightarrow & CaO & + & CO_2 \\
(40+12+48) & & & & \text{22·4 litres} \\
=100 & & & & \text{at N.T.P.} \\
MgCO_3 & \rightarrow & MgO & + & CO_2 \\
(24+12+48) & & & & \text{22·4 litre} \\
=84 & & & & \text{at N.T.P.}
\end{array}
$$
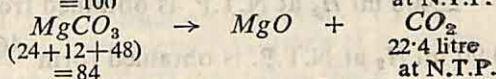
∵   100 g of $CaCO_3$ gives 22·4 litres of CO_2 at N.T.P.,

∴ x g of $CaCO_3$ gives $\dfrac{22·4 \times x}{100}$ litres at N.T.P.

Again,   ∵   84 g of $MgCO_3$ gives 22·4 litre of CO_2 at N.T.P.,

∴ $(1-x)$ of $MgCO_3$ gives $\dfrac{22·4\,(1-x)}{84}$ litre at N.T.P.

∴ $\dfrac{22·4 \times x}{100} + \dfrac{22·4\,(1-x)}{84} = \dfrac{240}{1000}$

or $\dfrac{22·4}{4}\left[\dfrac{x}{25} + \dfrac{1-x}{21}\right] = 0·24$

or $\dfrac{x}{25} + \dfrac{1-x}{21} = \dfrac{0·24 \times 4}{22·4}$

or $\dfrac{21x + 25 - 25x}{525} = 0·0428$,   or $-4x + 25 = 525 \times 0·0428$

or $-4x = 22 \cdot 47 - 25$
or $-4x = -2 \cdot 53$
or $x = 0 \cdot 632 = $ wt. of $CaCO_3$
∴   Wt. of $MgCO_3 = 1 - 0 \cdot 632 = 0 \cdot 368$.
∴   % of $CaCO_3 = 63 \cdot 2\%$
      % of $MgCO_3 = 36 \cdot 8\%$.

8.   1 g of sodium amalgam on treatment with water gives 200 ml of Hydrogen at 13°C and 76 cm pressure. Find the percentage of sodium in the amalgam.

Solution :

$$2Na \;+\; 2H_2O \;\rightarrow\; 2NaOH \;+\; \underset{\substack{22 \cdot 4 \text{ litres} \\ \text{at N.T.P.}}}{H_2}$$
$$\underset{=46}{2 \times 23}$$
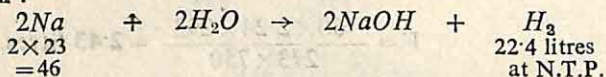
Volume of $H_2 = 200$ ml
Pressure $= 76$ cm
Temp. $= 13°C = 273 + 13 = 286$ K.

Let the voulme of this H_2 at N.T.P. be V ml.

$$\therefore \quad \frac{76 \times V}{273} = \frac{76 \times 200}{286}$$

$$\therefore \qquad V = \frac{200 \times 273}{285} \text{ ml}$$

$$= 190 \cdot 90 \text{ ml}.$$

Now, ∵   22400 ml H_2 at N.T.P. is obtained from 46 g sodium,

∴   190·90 ml H_2 at N.T.P. is obtained form $\dfrac{46 \times 190 \cdot 90}{22400}$ g Na

$$= 0 \cdot 392 \text{ g } Na.$$

Thus, 0·392 g Na is present in 1 g amalgam.
∴   % of $Na = 39 \cdot 2\%$.

9.   1·15 g of metallic sodium reacts with excess of water. What is the volume of hydrogen evolved at S T.P. ?
(Atomic masses in amu are $Na = 23$, $H = 1$, $O = 16$)

Solution : $$2Na \;+\; 2H_2O \;\rightarrow\; 2NaOH \;+\; \underset{\substack{22 \cdot 4 \text{ litres} \\ \text{at S.T.P.}}}{H_2}$$
$$\underset{=46}{2 \times 23}$$
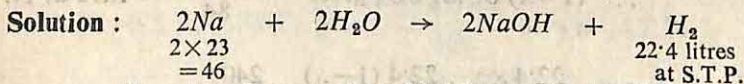
∵   46 g of sodium evolves 22·4 litres H_2 at S.T.P.,

∴   1·15 g of sodium evolves $\dfrac{22 \cdot 4 \times 1 \cdot 15}{46}$ litre H_2

$$= 0 \cdot 56 \text{ litre} = 560 \text{ ml}.$$

(C) Calculations involving Volume-Volume :

(EUDIOMETRY)

The study concerning calculations involving volumes of gases taking part in a chemical reaction is known as **Eudiometry**.

In chemical reactions in which the reactants and the products both are gaseous, we do not have to deal with their actual **volumes**, rather with the **relation between these volumes.** Hence, we generally take 1 gram molecule of a gas at N.T.P. to be 1 volume, instead of taking 22·4 litres.

$$H_2 \quad + \quad Cl_2 \quad \rightarrow \quad 2HCl$$
$$\text{1 vol.} \qquad \text{1 vol.} \qquad \text{2 volumes}$$
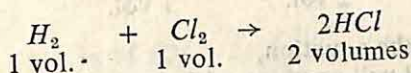
In these calculations it is important to note the following points :

(i) The volume ratio of two gases may be taken as their molar ratio.

Thus,
$$H_2 \quad + \quad Cl_2 \quad \rightarrow \quad 2HCl$$
$$\begin{array}{ccc} \text{1 volume} & \text{1 volume} & \text{2 volumes} \\ \text{1 mole} & \text{1 mole} & \text{2 moles} \end{array}$$
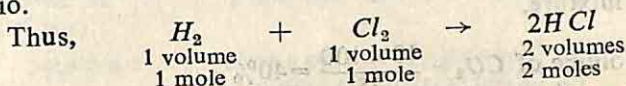
(ii) A chemical equation represents the reaction at N.T.P.

(iii) 1 gram-molecule of any gas at N.T.P. is assumed to occupy 1 volume (i.e., 22·4 litres).

(iv) The molecular weight of a gas is twice its vapour density.

(v) Hydrogen and oxygen combine together to form steam, which is then liquefied into liquid water.

$$2H_2 \quad + \quad O_2 \quad \rightarrow \quad 2H_2O \text{ (liquid)}$$
$$\text{2 vol.} \qquad \text{1 vol.} \qquad \text{0 vol.}$$
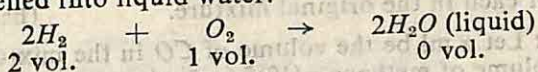
In this case, contraction in volume $= 3$ vol.
$$1/3 \text{ of contraction} = \text{volume of oxygen.}$$
$$2/3 \text{ of contraction} = \text{volume of hydrogen.}$$

(vi) The absorption of CO_2 gas takes place in $NaOH$ or KOH solution, whereas O_2 is absorbed by alkaline pyrogallol solution.

Solved Problems

1. What volume of CO can be obtained theoretically from 100 litres of CO_2, both measured under the same conditions of temperature and pressure ?

Solution :
$$CO_2 \quad + \quad C \quad \rightarrow \quad 2CO$$
$$\begin{array}{cc} \text{1 vol.} & \text{2 vol.} \\ \text{1 litre} & \text{2 litres} \end{array}$$

or

∴ 1 litre of CO_2 gas gives 2 litres of CO gas,

∴ 100 litres of CO_2 gas gives $2 \times 100 = 200$ litres of CO gas.

2. What volume of oxygen would be required to burn completely 100 ml of acetylene at N.T.P. ?

Solution :
$$2C_2H_2 \quad + \quad 5O_2 \quad \rightarrow \quad 4CO_2 \quad + \quad 2H_2O$$
$$\text{2 vol.} \qquad \text{5 vol.} \qquad \text{4 vol.}$$
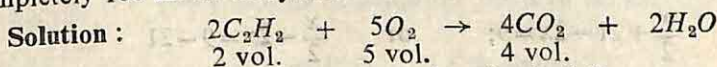
Thus, ∵ 2 ml of acetylene requires 5 ml of O_2,

∴ 100 ml of acetylene requires $\dfrac{5 \times 100}{2}$ ml of O_2

$$= 250 \text{ ml of } O_2$$

3. 10 ml of carbon monoxide are exploded with 20 ml of oxygen in an eudiometer tube over mercury. What volume of gas is left and what is its composition ?

Solution :

$$2CO + O_2 \rightarrow 2CO_2$$
$$2 \text{ vol.} \qquad 1 \text{ vol.} \qquad 2 \text{ vol.}$$
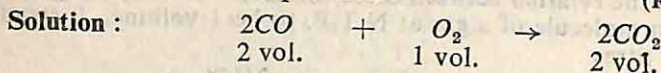
According to the equation,

10 ml of CO will combine with 5 ml of O_2 to give 10 ml CO_2.

∴   Volume of O_2 left unused $= 20 - 5 = 15$ ml
    Volume of CO_2 formed $= 10$ ml.

∴   Total volume of gas after the reaction $= 15 + 10 = 25$ ml.

∴   In the mixture,

$$\text{Volume of } CO_2 = \frac{10 \times 100}{25} = 40\%$$

$$\text{Volume of } O_2 = \frac{15 \times 100}{25} = 60\%.$$

4. 9·0 ml of oxygen is required for complete combustion of 10·5 ml of a mixture of carbon monoxide and methane. Calculate the percentage of each in the original mixture.

Solution : Let x ml be the volume of CO in the mixture.

∴   Volume of methane $= (10·5 - x)$ ml

$$2CO + O_2 \rightarrow 2CO_2$$
$$2 \text{ ml} \quad 1 \text{ ml}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$1 \text{ ml} \quad 2 \text{ ml}$$
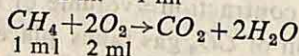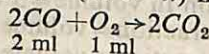
Now, ∵ 2 ml of CO requires 1 ml of O_2,

∴ x ,,   ,, $\dfrac{x}{2}$,,   ,,

Again, ∵ 1 ml of CH_4 requires 2 ml of O_2,

∴ $(10·5 - x)$ ml ,,   ,, $2(10·5 - x)$ ml of O_2

∴ Total volume of $O_2 = \left[\dfrac{x}{2} + 2(10·5 - x) \right]$ ml.

Thus, $\dfrac{x}{2} + 2(10·5 - x) = 9·0$

or $\dfrac{x}{2} + 21 - 2x = 9;$ or $\dfrac{x}{2} - 2x = 9 - 21$

or $\dfrac{x - 4x}{2} = -12;$ or $x - 4x = -24$

or $-3x = -24;$ or $x = \frac{24}{8} = 8$ ml

i.e.   volume of $CO = 8$ ml

∴   volume of $CH_4 = 10.5 - 8 = 2.5$ ml

∴   % of $CO = \dfrac{8 \times 100}{10.5} = 76.19\%$

and   % of $CH_4 = \dfrac{2.5 \times 100}{10.5} = 23.81\%$.

5. When 15 ml of a mixture of oxygen and nitrogen mixed with 30 ml of hydrogen at 25°C are exploded, 27 ml of gas is left on cooling to 25°C. Find out the percentage composition of the mixture.   (R. U. 1975 A)

Solution :   Volume of the mixture $= 15$ ml
                        Volume of hydrogen $= 30$ ml
                        Volume after explosion $= 27$ ml.
∴   Contraction in volume $= (15 + 30) - 27 = 18$ ml.

This contraction in volume is due to the formation of water by the combination of H_2 and O_2.

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$2 \text{ ml} \quad 1 \text{ ml} \quad 0 \text{ ml}$$
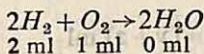
          Contraction $= 3$ ml.
∵   3 ml contraction is due to 1 ml O_2,
∴   18 ,,   ,,   ,, $\dfrac{1 \times 18}{3}$ ml O_2

                                    $= 6$ ml O_2
∴   Volume of $N_2 = 15 - 6 = 9$ ml
Thus,   % volume of $O_2 = 40\%$
               %   ,, $N_2 = 60\%$.

6. Find the resultant volumes measured at the temperature and pressure when (a) 10 ml of carbon monoxide are exploded with 25 ml of oxygen, and (b) 10 ml of oxygen are exploded with 25 ml of carbon monoxide.   (I.I.T. Adm. Test)

Solution : (a) $2CO + O_2 \rightarrow 2CO_2$
                                 $2 \text{ ml} \quad 1 \text{ ml} \quad 2 \text{ ml}$

∵ 2 ml of CO combines with 1 ml of O_2 to give 2 ml of CO_2,
∴ 10 ml   ,,   ,,   5 ml   ,,   ,,   10 ml CO_2
∴   Volume of oxygen left unused $= (25 - 5)$ ml $= 20$ ml
∴   Total volume of resultant gas $= 10$ ml $CO_2 + 20$ ml O_2
                                     $= 30$ ml.

(b) ∵ 1 ml O_2 combines with 2 ml CO giving 2 ml CO_2,
∴ 10   ,,   ,,   20 ml ,,   20 ml ,,
∴ CO left unused $= 25 - 20 = 5$ ml
∴ Volume of resultant gases $= 20$ ml $CO_2 + 5$ ml CO
                             $= 25$ ml.

7. 10 ml of a mixture of H_2, CO and CO_2 are mixed with 15 ml of Oxygen. The resultant mixture of gases was exploded. The resulting mixture of gases was then cooled to the original room temperature and pressure and was found to measure 19 ml. On shaking with caustic potash solution a further contraction to 12 ml took place. Deduce the percentage composition of the mixture.

Solution : Let the volumes of H_2, CO and CO_2 in the mixture be x ml, y ml and z ml respectively.

On explosion the reactions occurring are :

(i)
$$2H_2 + O_2 \rightarrow 2H_2O$$
$$\text{2 ml} \quad \text{1 ml}$$
$$x \text{ ml} \quad x/2 \text{ ml}$$

(ii)
$$2CO + O_2 \rightarrow 2CO_2$$
$$\text{2 ml} \quad \text{1 ml} \quad \text{2 ml}$$
$$y \text{ ml} \quad y/2 \text{ ml} \quad y \text{ ml}$$
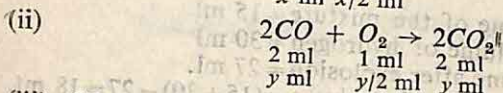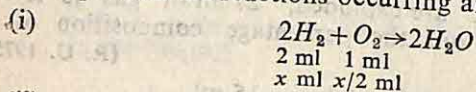
(iii) CO_2 is left unreacted. This is z ml.

Contraction on shaking with KOH is due to the absorption of CO_2.

$$\text{Volume of } CO_2 = (y+z) \text{ ml}$$

But,
$$y+z = 19-12 = 7$$

$$\therefore \quad x+y+z = 10 \text{ ml} \qquad \qquad \cdots \text{(a)}$$

$$\therefore \quad x+7 = 10; \qquad \text{or} \qquad x = 10-7 = 3 \text{ ml}$$

Volume of O_2 used $= \dfrac{x}{2} + \dfrac{y}{2} = 15 - 12 = 3$ ml

i.e.,
$$\frac{x}{2} + \frac{y}{2} = 3; \qquad \text{or} \qquad \frac{3}{2} + \frac{y}{2} = 3$$

or $y/2 = 3 - 3/2 = 3/2;$ or $y = 3.$

Now, $x+y+z = 10$

or $3+3+z = 10;$ $\therefore \quad z = 4$

i.e.,   Volume of $H_2 = 3$ ml
         Volume of $CO = 3$ ml
         Volume of $CO_2 = 4$ ml

$\therefore$ Percentage of $H_2 = 30\%$
         ,, $CO = 30\%$
         ,, $CO_2 = 40\%$.

8. 10 ml of methane are mixed with 25 ml of O_2 in an eudiometer and exploded. A piece of solid KOH is then introduced into the tube to absorb completely the CO_2 produced. Find the volume of the residual gas and calculate the volume of CO_2 produced.

Solution :
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$\text{1 ml} \quad \text{2 ml} \quad \text{1 ml}$$
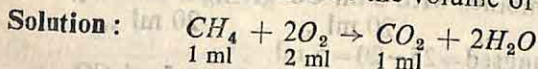
$\therefore$ 1 ml of CH_4 requires 2 ml of O_2 to give 1 ml of CO_2,
$\therefore$ 10 ml   ,,   ,,   20 ml   ,,   ,, 10 ml   ,,

∴   Volume of CO_2 absorbed by $KOH = 10$ ml
           Volume of O_2 left unused $= 25 - 20 = 5$ ml.

9. 10 ml of mixture of N_2O and NO are mixed with 200 ml of H_2 and exploded. 80 ml of N_2 remained. Find the composition of the mixture.

Solution : Let x ml be the volume of N_2O.
∴   Volume of $NO = (100 - x)$ ml

$$N_2O \ + \ H_2 \ \to \ H_2O \ + \ N_2$$
$$\text{1 ml} \quad \text{1 ml} \quad \text{0 ml} \quad \text{1 ml}$$
$$2NO \ + \ 2H_2 \ \to \ 2H_2O \ + \ N_2$$
$$\text{2 ml} \quad \text{2 ml} \quad \text{0 ml} \quad \text{1 ml}$$
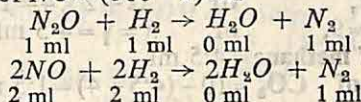
∵   1 ml of N_2O gives 1 ml of N_2,
∴ x ml   ,,   ,,   ,, x ml   ,,
Again, ∵ 2 ml of NO gives 1 ml of N_2,

∴ $(100 - x)$ ml of NO will give $\dfrac{(100 - x)}{2}$ ml of N_2.

But, total volume of N_2 formed $= 80$ ml

∴ $x + \dfrac{100 - x}{2} = 80;$ or $2x + 100 - x = 160$

or $x = 60$ ml $=$ volume of N_2O
∴   Volume of $NO = 100 - 60 = 40$ ml.
Thus, $N_2O = 60$ ml; $NO = 40$ ml.

10. 10 ml of a mixture of Methane, Ethylene and Carbon dioxide were exploded with excess of air. After explosion, there was a contraction of 17 ml, and after treatment with KOH there was further contraction of 14 ml. What was the composition of the mixture ?

Solution : Let the volumes of Methane and Ethylene in the mixture be x ml and y ml respectively.
∴   Volume of carbon dioxide $= 10 - (x + y)$

$$CH_4 \ + \ 2O_2 \ \to \ CO_2 \ + \ 2H_2O$$
$$\text{1 ml} \quad \text{2 ml} \quad \text{1 ml} \quad \text{0 ml} \qquad \text{Contraction} = 2 \text{ ml}$$
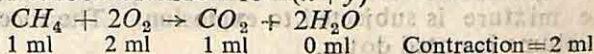
For 1 ml of methane the contraction is 2 ml, hence for x ml of methane, contraction $= 2x$ ml.
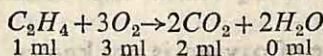
$$C_2H_4 + 3O_2 \to 2CO_2 + 2H_2O$$
$$\text{1 ml} \quad \text{3 ml} \quad \text{2 ml} \quad \text{0 ml}$$
$$\text{Contraction} = 2 \text{ ml}$$

For 1 ml C_2H_4 the contraction is 2 ml
∴   for y ,,   ,,   ,, $2y$ ml
∴   Total first contraction $= (2x + 2y)$ ml
Hence, by the question,

$$2x + 2y = 17.$$
Now, ∵   1 ml CH_4 gives 1 ml CO_2,
∴ x ,,   ,, x ,,   ,,

Again,   1 ml C_2H_4 gives 2 ml CO_2,

∴ y „   „   „ 2y ml CO_2

∴   Total CO_2 formed $= (x+2y)$ ml

CO_2 initially present $= 10-(x+y)$

∴ $10-(x+y)+x+2y=14$

or $10-x-y+x+2y=14$;   or $y=4$

i.e.,   Volume of Ethylene $= 4$ ml

∵ $2x+2y=17$,   or $2x+2 \times 4 = 17$

or $2x=17-8=9$,   or $x = \frac{9}{2} = 4 \cdot 5$ ml

i.e.,   **Volume of methane** $= 4 \cdot 5$ ml

∴   **Volume of** $CO_2 = 10-(4 \cdot 5+4) = 1 \cdot 5$ ml.

11. 50 volumes of a gas mixed with 70 volumes of oxygen give after explosion 50 volumes of Carbon dioxide and after absorption by *KOH*, 45 volumes Oxygen are left. What is the gas ?

<div align="right">(I.I.T. Adm. Test)</div>

Solution : Volume of the gas $= 50$ vol.

Volume of O_2 added $= 70$ vol.

Volume of CO_2 produced $= 50$ vol

Volume of O_2 left $= 45$ vol.

Volume of O_2 consumed in combustion $= 70-45 = 25$ vol.

∴   50 volumes of the gas combine with 25 volumes of O_2 to form 50 volumes of CO_2.

or   2 volumes of the gas combines with 1 volume of O_2 to form 2 volumes of CO_2.

or   2 molecules of gas combines with 1 molecule of O_2 to form 2 molecules of CO_2.

∴   2 molecules of gas $= 2CO_2 - O_2 = 2CO$

i.e.,   Formula of the gas is **CO**.

Molecular formula of Hydrocarbons :

In order to determine the molecular formula of a gaseous hydro-carbon, a **known volume of it** is mixed up with an **excess of oxygen**. The mixture is subjected to **explosion.** The successive contraction in volume is noted down.

Three cases may arise :

(i) When the volume of O_2 added and contractions in volume are known.

(ii) When the volume of oxygen is not known, but contractions in volume are known. The density of the hydrocarbon is not given.

(iii) When the volume of O_2 added is not known. First contrac-tion is known. The density of the gas is given.

Solved Problems

12. 5 ml of a gas containing Carbon and Hydrogen only were mixed with 30 ml of Oxygen and the mixture subjected to electric discharge. After explosion the volume was 25 ml. On treatment

with conc. *KOH* solution the volume was reduced to 15 ml. The remaining gas was pure oxygen. Find the molecular formula of the hydrocarbon. (All volumes are measured at N.T.P.) **(I.I.T. 1979)**

Solution : The gas is a hydrocarbon.

Volume of the hydrocarbon = 5 ml

Volume of O_2 added = 30 ml

Volume of the mixture after explosion = 25 ml

Volume of gas absorbed by KOH = Volume of CO_2

= 25 − 15 = 10 ml

Volume of unused O_2 = 15 ml

∴   Volume of O_2 consumed = 30 − 15 = 15 ml

Let the formula of the Hydrocarbon be C_xH_y.

It will react with oxygen as follows :

$$C_xH_y + (x+y/4) O_2 \rightarrow xCO_2 + y/2\ H_2O$$
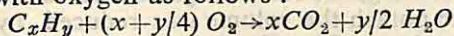
1 ml $(x+y/4)$ ml x ml

∴   5 ml $5(x+y/4)$ ml $5x$ ml

Volume of CO_2 formed = $5x$ ml

∴ $5x = 10$;   or $x = 2$

Volume of O_2 used = $5(x+y/4)$

∴ $5(x+y/4) = 15$;   or $x+y/4 = 3$

or $2+y/4 = 3$;   or $y/4 = 1$;   or $y = 4$

i.e.,   Molecular formula of Hydrocarbon is C_2H_4.

13. 20 ml of a gaseous Hydrocarbon were exploded with excess of oxygen and cooled. There was a contraction of 40 ml. On treatment with *KOH* there was a further contraction of 40 ml. What was the Hydrocarbon ?

Solution : Volume of Hydrocarbon = 20 ml

First contraction = 40 ml

Second contraction = 40 ml

Let the formula of the Hydrocarbon be C_xH_y.

Now, $C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2\ H_2O$

1 ml $(x+y/4)$ ml x ml

∴   20 ml $20(x+y/4)$ ml $20x$ ml

Volume of CO_2 = Second contraction

$$= 40\ ml; \quad \therefore \quad 20x = 40, \quad or \quad x = \frac{40}{20} = 2.,$$

Now, Volume of Hydrocarbon + Volume of O_2 used

= First contraction + Second contraction

or   20 + Volume of O_2 used = 40 + 40

or   Volume of O_2 used = 60 ml.

∴ $20(x+y/4) = 60$;   or $20(2+y/4) = 60$

or $2+y/4 = 3$;   or $y/4 = 1$;   or $y = 4$.

∴   Molecular formula of the Hydrocarbon is C_2H_4.

14. 20 ml of a gaseous Hydrocarbon are exploded with Oxygen avoiding excess. On cooling the volume contracts by 60 ml. The density of the Hydrocarbon is 22. Find the formula.

Solution : $C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2\ H_2O$
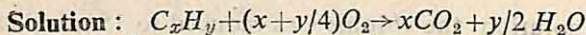
Volume of O_2 used up to combine with H_2 only $= 60 - 20$

$= 40$ ml

$\therefore$ Volume of H_2 present in 20 ml Hydrocarbon $= 80$ ml

Hence, 1 vol of C_xH_y contains 4 vol of hydrogen

or 'n' molecule of C_xH_y contains $4n$ molecules of hydrogen

or 1 molecule of C_xH_y contains 8 atoms of hydrogen

$\therefore$ Formula is C_xH_8. $\therefore$ Formula wt. $= 12x + 8$

Molecular   weight $= 2 \times 22 = 44$; $\therefore$ $12x + 8 = 44$

or $12x = 44 - 8 = 36$;   or $x = 3$.

$\therefore$ Formula of Hydrocarbon is C_3H_8.

15. 20 ml of Hydrocarbon C_xH_y are exploded with 200 ml of Oxygen. After cooling, the residual gas occupied 190 ml. On treatment with caustic potash the volume was reduced by 40 ml. Find the value of x and y. Give the I. U. P. A. C. name of the Hydrocarbon.

Solution : Volume of the Hydrocarbon $= 20$ ml

Volume of Oxygen added $= 200$ ml

Total volume before explosion $= (20 + 200)$ ml $= 220$ ml.

Volume after explosion $= 190$ ml

$\therefore$ First contraction $= (220 - 190) = 30$ ml.

Second contraction $= 40$ ml.

$C_xH_y\ (x+y/4)O_2 \rightarrow xCO_2 + y/2\ H_2O$
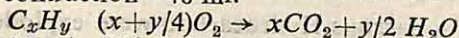
20 ml $20(x+y/4)$ ml $20x$ ml

Second contraction $=$ Volume of CO_2 formed.

$\therefore$ $40 = 20x$; $\therefore$ $x = 2$

Volume of Hydrocarbon $+$ Volume of O_2 used

$=$ First contraction $+$ Second contraction

$\therefore$ 20 $+$ volume of O_2 used $= 30 + 40$

or   volume of O_2 used $= (30 + 40) - 20 = 50$ ml

i.e., $20(x + y/4) = 50$;   or $20(2 + y/4) = 50$

or $40 + 5y = 50$;   or $y = 2$

$\therefore$ Formula of Hydrocarbon is C_2H_2.

I. U. P. A. C. name : Ethyne

16. 500 ml of a gaseous Hydrocarbon burnt in excess of Oxygen gave 2500 ml of Carbon dioxide and 3 litres of water vapour, all volume being measured at the same temperature and pressure. What is the formula of the Hydrocarbon ?

Solution : Let the formula of the Hydrocarbon be C_xH_y.

$C_xH_y\ \ +\ \ (x+y/4)O_2 \longrightarrow xCO_2\ +\ \ y/2\ H_2O$
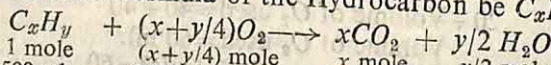
1 mole $(x+y/4)$ mole x mole $y/2$ mole

500 ml $500(x+y/4)$ ml $500x$ ml $500 \times y/2$ ml

Thus, volume of CO_2 formed $= 500x$ ml

$\therefore$ $500x = 2500$;   or $x = 5$

Volume of water-vapour formed $= 500 \times y/2$ ml

$\therefore$ $500 \times y/2 = 3000$;   or $y = 12$.

$\therefore$ Formula of the Hydrocarbon is C_5H_{12}.

Questions

Long Answer Type :

1. What is the difference between an empirical formula and a molecular formula ?

2. How would you deduce the empirical formula from the percentage composition of the compound ?

Short Answer Type :

1. What is a simple formula ?
2. What do you mean by a molecular formula ?
3. What is eudiometry ?
4. Which products are obtained when a hydrocarbon is burnt in air ? Give a general equation.

Problems :

1. Calculate the simplest empirical formulae for the substances with the following analyses by weight :

(a) $75.00\% \; C, \; 25.00\% \; H.$
(b) $6.25\% \; H, \; 43.75\% \; N, \; 50.0\% \; O.$

2. The percentage composition of a compound is found to be the following :

$C=40\%, \; H=6.64\%$ and $O=53.33\%.$

Find the empirical formula of the compound.

3. The percentage composition of an acid is the following :

$H=2.04\%, \; S=32.65\%$ and $O=65.31\%.$

The molecular weight of the acid is 98. Find the molecular formula of the acid.

4. How much ethyl alcohol could be produced by the fermentation of 1·00 kg of sugar by the reaction

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \; ?$$
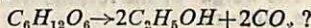
5. What weight of N_2 will be required to produce 34·0 g of NH_3 by the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$?   (**Ans.** 28·0 g N_2)

6. What weight of KI is needed to produce 20·00 g of I_2 by the reaction

$$5KI + KIO_3 + 6HNO_3 \rightarrow 6KNO_3 + 3I_2 + 3H_2O \; ? \quad (\textbf{Ans.} \; 10·9 \; g \; KI)$$
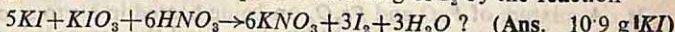
7. A mixture of $NaCl$ and $NaBr$ is dissolved in water and treated with $AgNO_3$ to give a precipitate of $AgCl$ and $AgBr$. After filtration and drying the mixture of $AgCl$ and $AgBr$ is found to weigh 9·00 g. The mixture is heated in a stream of Cl_2 giving the reaction

$$2AgBr + Cl_2 \rightarrow 2AgCl + Br_2.$$
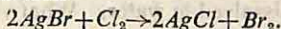
The solid then weighs 8·00 g. What was the weight of $NaBr$ in the original mixture ?

8. A mixture of sodium bicarbonate ($NaHCO_3$) and sodium carbonate decahydrate ($Na_2CO_3.10H_2O$) is heated forming sodium carbonate (Na_2CO_3) from both compounds. The reactions are :

$$Na_2CO_3 10H_2O \rightarrow Na_2CO_3 + 10H_2O$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$
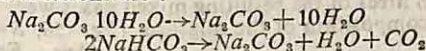
If 1·100 g of dry CO_2 are formed and the total weight loss of CO_2 and H_2O from the mixture is 4·000 g, what was the original weight of $Na_2CO_3.10H_2O$?   (**Ans.** 5·64 g $Na_2CO_3.10H_2O$)

9. Chlorine may be prepared by oxidation of the chloride ion by MnO_2 in the reaction

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2.$$
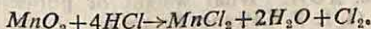
What is the maximum volume of chlorine at N.T.P. that can be obtained from 100 g of MnO_2 ?   (Ans. 25·8 litres)

10. What volume of oxygen collected at N.T.P. is given off on heating 1 g of mercuric oxide ?   (Ans. 0·0518 litre)

11. How much H_2SO_4 is required to decompose 100 g of chalk and how much calcium sulphate will we produced ?   (Ans. 98 g; 136 g)

12. Calculate the weight of iron converted into oxide by the action of 18 g of steam.   (Ans. 42 g)

13. 1·4 g of copper is displaced from a solution of copper sulphate in water by iron. Find the weight of ferrous sulphate formed ($Cu=63·5$). (Ans. 3·351 g)

14. Calculate the weight of pyrolusite containing 80% MnO_2 which must react with HCl to obtain as much chlorine as to completely combine with H_2 evolved by the action of dil. HCl on 10 g of Magnesium ($Mn=55$).

(Ans. 45·312 g)

15. A quantity of a mixture of KI and $NaCl$ converted into the normal sulphate is found to weigh the same as the original salts. Find the composition of the mixture.   (Ans. $KI=30·98$; $NaCl=69·02$)

16. 0·6 g of a sample of sodium chloride when treated with $AgNO_3$ solution gave 1·37 g $AgCl$. Calculate the percentage of purity of sample of sodium chloride.   (Ans. 93·1%)

17. Calculate the amount of calcium carbonate which must be decomposed by HCl to produce as much CO_2 as would suffice to convert 30 g of caustic soda into sodium carbonate.   (Ans. 37·5 g)

18. 1 g of a mixture of KCl and KI was dissolved in water and treated with $AgNO_3$ solution. The precipitate was found to weigh 1·618 g. Calculate the percentage of each in the mixture. ($K=39$, $Cl=35·5$, $I=127$, $Ag=108$)
(Ans. $KCl=39·7$%; $KI=60·3$%)

19. 4·5 g of a mixture of $NaHCO_3$ and Na_2CO_3 was heated strongly to give a constant weight of residue. The weight of the residue was 4·105 g. Calculate the percentage composition of the mixture.

20. 1·84 g of a mixture of $CaCO_3$ and $MgCO_3$ were heated till the final weight was constant. The residue was found to weigh 0·96 g. Find the weight of both the salts in the mixture.   (Ans. $CaCO_3=1$ g, $MgCO_3=0·84$ g)

21. A mixture of FeO and Fe_3O_4 on being heated in air to a constant weight was found to be increased in weight by 5%. Find the composition of the original mixture.   (I. I. T. 1978) (Ans. $FeO=20·2$%; $Fe_3O_4=79·8$%)

22. What weight of ammonium chloride would be required to prepare 10 litres of ammonia at N. T. P. ?   (Bhag. U. 1974A) (Ans. 23·88 g)

23. 70 g of Bromine are dissolved in water. What volume of H_2S at 15°C is required to convert it into HBr ?   (Ans. 10·33 litres)

24. You are given a balloon with a capacity of 10^3 litre and you wish to fill it with Hydrogen at 30°C and 750 mm pressure. How much iron would you require for the purpose ?   (Ans. 2222·83 g)

25. 10 g of a mixture of iron sulphide and iron were treated with dilute sulphuric acid when 3·36 litres of the resulting mixed gases were obtained at N. T. P. Find the percentage composition of the mixture. ($Fe=56$, $S=32$). (R. U. 1969A)
(Ans. $FeS=62$%, $Fe=38$%)

26. 5·08 g of Iodine suspended in water is treated slowly with 460 ml of H_2S at N.T.P. Find the weight of sulphur liberated. ($I=127$, $S=32$) (R. U. 1973 A)
(Ans. 0·64 g)

27. 5 litres of chlorine at 5°C and 762 mm pressure is passed into (a) cold dilute KOH, (b) hot conc. KOH. What weight of potassium chloride will be obtained ?   (I. I. T. Entrance Exam.)   [Ans. (a) 16·37g, (b) 27·28g]

28. 1g of a sample of $KClO_3$ is heated in such a way that a part of it decomposes according to equation (i) and the remaining portion decomposes according

to equation (ii).

$$2KClO_3 \rightarrow 2KCl + 3O_2 \qquad \cdots \text{ (i)}$$
$$4KClO_3 \rightarrow 3KClO_4 + KCl \qquad \cdots \text{ (ii)}$$

If the volume of oxygen evolved at N.T.P. is 146·8 ml, calculate the percentage weight of $KClO_4$ in the residue. (I. I. T. 1977)

29. What volume of chlorine at 12°C and 780 mm pressure will be obtained when 110 g of Manganese dioxide react with conc. HCl ? If the acid contains 38% HCl and has a specific gravity of 1·2, what volume of it will then be required ? $(Mn=55, Cl=35·5, O=16)$ (Ans. 28·8 litres; 404·8 ml)

30. What volume of CO_2 at N.T.P. will be obtained by the action of 10 litres of HCl (sp. gr. 1·16) containing 30% of the acid by weight on 50 kg of Na_2CO_3 ? (Ans. 1067·8 litres at N.T.P.)

31. 100 ml of Carbon monoxide are mixed with 40 ml of Oxygen and exploded If the resulting mixture is shaken with Caustic potash, what volume of the gas will remain and what gas will it be ? (Ans. 20 ml of CO)

32 10 ml of a mixture of N_2 and O_2 were mixed with 20 ml of H_2 and the mixture was exploded. The volume after explosion was found to be 21 ml (measured at the initial temperature and pressure). Calculate the volume percentage of the mixture. (Ans. $O_2 = 30\%$, $N_2 = 70\%$)

33. 20 ml of an equimolecular mixture of Methane and a gaseous compound of Acetylene series were mixed with 100 ml of Oxygen and exploded. The volume of the product after cooling to original room temperature and pressure was 80 ml, and on treatment with Potash solution a further contraction of 40 ml was observed. Calculate the molecular formula of the Hydrocarbon. (Ans. C_3H_4)

34. 20 ml of a mixture of CH_4 and H_2 is mixed with 30 ml Oxygen and exploded. On cooling the volume becomes 15 ml, and on treatment with KOH the volume becomes 5 ml, all measured at N.T.P. What weight of each gas did the original mixture contain ?

Solution : Let the volume of $CH_4 = x$ ml
$$\therefore \quad \text{Vol. of } H_2 = (20-x) \text{ ml}$$
Volume of O_2 left unused $= 5$ ml
$$\therefore \quad \text{Volume of } O_2 \text{ used up} = 30 - 5 = 25 \text{ ml}$$
$$2H_2 + O_2 \rightarrow 2H_2O$$
$$\text{2vol} \quad \text{1vol}$$
$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$
$$\text{1vol} \quad \text{2vol}$$
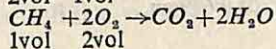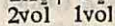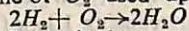
Volume of O_2 taken up by $(20-x)$ ml $H_2 = \left(\dfrac{20-x}{2}\right)$ ml

Volume of O_2 taken up by x ml $CH_4 = 2x$ ml

$$\therefore \quad 2x + \frac{20-x}{2} = 25$$

or $\quad x = 10$
$$\therefore \quad \text{Vol. of } CH_4 \text{ at N.T.P.} = 10 \text{ ml} = 10 \times 8 \times 0·00009$$
$$= 0·0072 \text{ g.}$$
$$\therefore \quad \text{Vol. of } H_2 \text{ at N.T.P.} = 10 \text{ ml} = 10 \times 0·00009$$
$$= 0·0009 \text{ g.]}$$

35. 10 ml of a gaseous Hydrocarbon were exploded with 33 ml of oxygen. After cooling the volume of the residual gases was 28 ml and on treating with KOH the volume decreased to 8 ml. Find the formula of the gas. (Ans. C_2H_2)

36. Find the molecular formula of Nitrogen peroxide at 154°C when its density is 25, given that 25 ml of the gas passed over heated copper gave 12·5 ml of Nitrogen. (Ans. NO_2)

37. A mixture of 5 ml of H_2, 5 ml of CH_4 and 15ml of oxygen is fired. Find the volume and composition of the residual gas. (Ans. $O_2 = 2·5$ ml, $CO_2 = 5$ ml)

Objective Questions :

(A) Select correct answer from each of the following questions :

1. The weight of 50% solution of HCl required to react with 100 g of $CaCO_3$ will be

(a) 73 g (b) 100 g (c) 146 g (d) 200 g.   (A. I. I. M. S. 1972)

2. 20 ml of carbon monoxide is burnt with 15 ml of oxygen. The volume of the residual oxygen will be (a) 35 ml (b) 5 ml (c) 10 ml (d) 20 ml.

3. 12 g of Magnesium is dissolved in excess of dil. H_2SO_4. The volume of Hydrogen evolved at N.T.P. is

(a) 22·4 litres (b) 44·8 litres (c) 11·2 litres (d) 1 ml.

4. The weight of iron required to be converted into Fe_3O_4 by 18 g of steam will be (a) 56 g (b) 168 g (c) 42 g (d) 18 g.

5. 1 mole of HCl is added to 2 moles of $AgNO_3$ in water. The amount of $AgCl$ precipitated will be :

(a) 1 mole (b) 2 moles (c) 0·5 mole (d) 3 moles.   (Poone 1974)

6. The amount of CO_2 required to convert 1 mole of $NaOH$ to Na_2CO_3 would be (a) 1 mole (b) 0·5 mole (c) 2 moles (d) 3 moles.

7. 18 g of water is electrolysed. Weight of oxygen obtained would be

(a) 8 g (b) 16 g (c) 32 g (d) 4 g.

8. The weight of Zn and H_2SO_4 needed to form H_2 to reduce completely 24 g of CuO ($M=79$) is

(a) 19·5 g of Zn and 29·7 g of H_2SO_4
(b) 20·7 g of Zn and 40 g of H_2SO_4
(c) 19·7 g of Zn and 34·7 g of H_2SO
(d) 29·7 g of Zn and 29·7 g of H_2SO_4.

9. 50 g of limestone are heated. Volume of CO_2 evolved at N.T.P. is

(a) 11·2 litres (b) 22·4 litres (c) 5·6 litres (d) 2·8 litres.

10. The amount of NH_4Cl required to yield 22·4 litres of NH_3 at N.T.P. will be

(a) 53·5 g (b) 107 g (c) 26·75 g (d) 40·0 g.

11. Hydrogen is made to react with CuO to form copper and water. What amount of hydrogen is required to produce 0·2 gm of Cu?

(a) 0·6299×10⁻³ gm (b) 6·299×10⁻³ gm (c) 62·99×10⁻³ gm (d) 629·9 gm.

12. How much iron can be theoritically otained by reducing 1 kg of Fe_2O_3 ?

(a) 699·3 gm (b) 69·93 gm (c) 6·993 gm (d) 0·699gm.

□□□

PROPERTIES OF GASES

Matter is known to exist in three states—**Solid, Liquid** and **Gas.**

Solid—A substance is said to be a solid if it melts above the room temperature under the atmospheric pressure.

A solid has a definite shape and volume.

Liquid—A substance is said to be in the liquid state when it freezes below the room temperature under atmospheric pressure.

The molecules in a liquid are not rigidly fixed. The forces of attraction holding the molecules are not so strong as in solids. Hence, a liquid has no definite shape.

The molecular forces are, however, strong enough to prevent their separation from one another. Hence, a liquid has a definite volume.

Gas—A substance is said to be in the gaseous state when it boils below the room temperature under atmospheric pressure.

The molecular forces of attraction in a gas are very much weaker. Hence, there are large inter-molecular voids. Therefore, the molecules of a gas can have translational, rotational and vibrational motions. The **density** of a gas is, therefore, low and its **compressibility** is high.

A gas has no bounding surface. Hence, it has neither a definite shape nor a definite volume.

The Gas Laws :

1. Boyle's Law—The law can be stated as follows :

The volume of a definite mass of a gas is inversely proportional to its pressure, at a constant temperature.

Thus, $P_1 \propto \dfrac{1}{V_1}$, at a constant temperature

or $P_1 = \dfrac{K}{V_1}$, where K is the constant of proportionality

or $P_1 V_1 = K$.

Similarly, if the pressure (P_1) of the gas changes to P_2 when the corresponding volume of the gas becomes V_2 at the same temperature, then,

$$P_2 V_2 = K$$
$$\therefore \quad P_1 V_1 = P_2 V_2 = \text{constant}$$

Boyle's Law may now also be expressed as :

The product of pressure and volume of a definite mass of a gas, at a fixed temperature, is a constant.[1]

A plot of P versus PV, at a given temperature, is a straight line parallel to the P-axis (see fig. below).
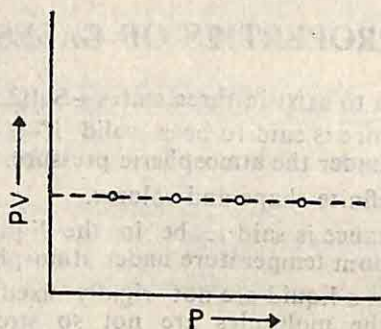
Similarly, a plot of P versus V, at a given temperature, is a rectangular hyperbola (see fig. below).
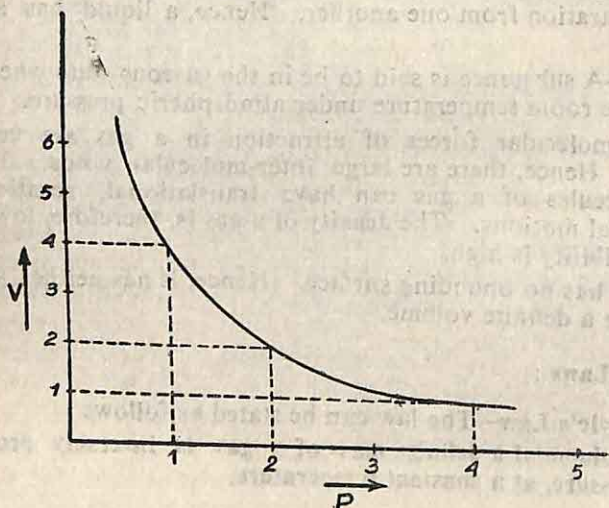
Relation between the Pressure and the Density of a gas, at a given temperature :

$$P_1V_1 = P_2V_2, \quad T \text{ being constant.}$$

Let the mass of the gas be M gram. If the densities of the gas at pressures P_1 and P_2 are D_1 and D_2 respectively, then,

$$V_1 = \frac{M}{D_1}, \text{ and } V_2 = \frac{M}{D_2}.$$

According to Boyle's law, $P_1V_1 = P_2V_2$.

$$\therefore \quad P_1 \times \frac{M}{D_1} = P_2 \times \frac{M}{D_2}, \qquad \text{or} \qquad \frac{P_1}{D_1} = \frac{P_2}{D_2}$$

i.e., $\qquad \dfrac{P}{D} = \text{constant;} \quad \text{or} \qquad P \propto D.$

Thus, at a given temperature, the pressure of a definite mass of a gas is directly proportional to its density.

2. **Charles' Law**—This law may be stated as follows :

For a given mass of a gas, at a constant pressure, the volume is directly proportional to the absolute temperature.

i.e., $\qquad\qquad\qquad V \propto T$ (at constant pressure)

or $\qquad\qquad\qquad V = KT$, where K is a constant.

At a constant pressure, if the volumes of a given mass of a gas are plotted against the corresponding absolute temperatures, the curves obtained should be straight lines. Such curves are known as **isobars**.

At $V = 0$, T is found to be $-273 \cdot 16°C$. This temperature is called **absolute zero**.
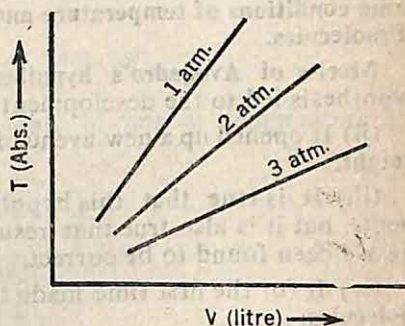
Absolute Scale of Temperature

(Kelvin Temperature)

Charles' Law may also be stated as follows :

The volume of a given mass of a gas increases or decreases by 1/273 of its volume at 0°C for every increase or decrease in temperature of 1°C, at a constant pressure.

Thus, 1 ml of a gas at 0°C becomes $(1 + \frac{1}{273})$ ml at 1°C

1 ml of a gas at 0°C becomes $(1 + \frac{2}{273})$ ml at 2°C

1 ml of a gas at 0°C becomes $(1 + \frac{5}{273})$ ml at 5°C

1 ml of a gas at 0°C becomes $\left(1 + \dfrac{t}{273}\right)$ ml at t°C

Similarly, 1 ml of a gas at 0°C becomes $(1 - \frac{1}{273})$ ml at -1°C

1 ml of a gas at 0°C becomes $(1 - \frac{5}{273})$ ml at -5°C

1 ml of a gas at 0°C becomes $(1 - \frac{273}{273})$ ml at -273°C

i.e., $\qquad$ 1 ml of a gas at 0°C becomes zero at -273°C

Thus, we see that the volume of a gas at -273°C vanishes. But nobody has as yet studied the volume of a gas to -273°C. All gases

become liquid before reaching this temperature. This temperature has, therefore, been adopted as the reference point in temperature-measurements and is called the **Absolute Zero.**

Thus,   0°C becomes 273° on absolute scale.
          100°C becomes $(273+100)=373°$ on absolute scale
i.e., $t°C = (273+t)°$ or $T°$ on absolute scale.

Temp. on the absolute scale is now generally written as T K (where, K indicates Kelvin).

3. Avogadro's hypothesis

Equal volumes of all gases (elementary or compound) under the same conditions of temperature and pressure contain the same number of molecules.

Merits of Avogadro's hypothesis—(i) The birth of Avogadro's hypothesis led to the development of Dalton's atomic theory.

(ii) It opened up a new avenue for the determination of molecular weight.

(iii) It is true that this hypothesis cannot be verified by experiments, but it is also true that results obtained on this basis have always been found to be correct.

(iv) It for the first time made the distinction between **atoms** and **molecules**.

(v) It explained clearly **Gay Lussac's Law of gaseous volumes.**
(vi) Besides these achievements, Avogadro's hypothesis led to the following important **deductions** :

Deductions—(A) The molecules of Hydrogen, Chlorine, Oxygen, Nitrogen and Fluorine are diatomic.

(B) The molecular weight of any gas is twice its density.

(C) The gram-molecular volume of all gases is the same under similar conditions of temperature and pressure and is 22·4 litre at N.T.P.

(D) It gave a method for the determination of the molecular formula of a gas from its volumetric composition.

(E) It provided a method for the determination of atomic weights of elements.

4. The Gas Equation (The combined gas law)—The combination of Boyle's law and Charles' law gives an equation relating the tempe-rature, pressure and volume of a definite mass of a gas. This equa-tion is known as the **Equation of State** for an ideal gas.

According to Boyle's law, $V \propto \dfrac{1}{P}$, when T is constant.

According to Charles' law, $V \propto T$, when P is constant,

Combining Boyle's and Charles' laws we get,

$V \propto \dfrac{T}{P}$, when T and P both vary;   or $\dfrac{PV}{T} = $ constant.

If the same number of moles of any gas at a given temperature and pressure is considered, the value of the constant will be the same, because equal number of molecules of different gases occupies the same volume under similar conditions of temperature and pressure. Thus, the constant is independent of the nature of the gas.

For 1 mole of a gas, $\dfrac{PV}{T} = $ universal constant (R), i.e.,

$$\frac{PV}{T} = R; \quad \text{or} \quad PV = RT.$$

Here, $V = $ volume occupied by 1 mole of gas at temperature T and pressure P.

Units of R :

(i) For one mole of gas, $PV = RT$.

$$\therefore \quad R = \frac{PV}{T}.$$

At N.T.P. (0°C and 1 atmospheric pressure), 1 mole of gas occupies 22·4 litres. Hence,

$$R = \frac{1 \times 22 \cdot 4}{273} = 0 \cdot 08205 \text{ litre-atm. deg}^{-1} \text{ mol}^{-1}.$$

(ii) In C.G.S. unit :

$$P = 1 \cdot 01325 \times 10^5 \text{ dyne cm}^{-2}$$
$$V = 22,400 \text{ ml}$$
$$T = 273 \text{ K}$$

$$\therefore \quad R = \frac{PV}{T} = \frac{1 \cdot 01325 \times 10^5 \text{ dyne cm}^{-2} \times 22,400 \text{ cm}^3}{1 \cdot 0 \text{ mole} \times 273 \text{ K}}$$

$$= 8 \cdot 31 \times 10^7 \text{ dyne cm K}^{-1} \text{ mole}^{-1}$$
$$= 8 \cdot 31 \times 10^7 \text{ erg K}^{-1} \text{ mole}^{-1} \text{ (dyne} \times \text{cm} = \text{erg).}$$

$$\therefore \quad 10^7 \text{ ergs} = 1 \text{ joule,}$$
$$\therefore \quad R = 8 \cdot 31 \text{ joule K}^{-1} \text{ mole}^{-1}$$
$$= 1 \cdot 988 \text{ cal K}^{-1} \text{ mole}^{-1} \text{ (4·18 joule} = 1 \text{ cal.)}$$

Calculation of Molecular mass :

Let the volume of a gas be v and suppose it contains n moles.

Then,
$$V = \frac{v}{n}$$

Putting this value of V in equation, $PV = RT$, we get

$$P \times \frac{v}{n} = RT; \qquad \text{or} \quad P_v = nRT.$$

Suppose, $m = $ mass of the gas
$M = $ Molecular mass

$$\therefore \qquad Pv = \frac{m}{M}.RT \qquad \left(\because \quad n = \frac{m}{M} \right)$$

or
$$\frac{m}{v} = \frac{PM}{RT}$$

or,
$$\rho = \frac{PM}{RT} \qquad (\rho = \text{density of the gas}).$$

So, if the density of a gas at a given temperature and pressure is known, the molecular mass of the gas can be calculated.

5. Gay-Lussac Law of Gaseous Volumes : According to this law, the volumes of gases, measured at the same temperature and pressure, taking part in a chemical reaction, are in the ratios of small whole numbers.

Thus, 1 volume of H_2 and 1 volume of Cl_2 combine to give 2 volumes of HCl.

$$H_2 + Cl_2 \rightarrow 2HCl$$
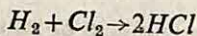
6. Dalton's Law of Partial Pressures : This law may be stated as—

When two or more gases, which do not react chemically with one another, are present in a definite volume, then, at a constant temperature, the total pressure exerted by the gaseous mixture is equal to the sum of the partial pressures which each gas would exert if it were left alone to occupy the same total volume.

Consider the gases A, B and C taken separately in a V litre flask at temperature T. Let P_A, P_B and P_C be the partial pressures of A, B and C respectively. If these gases are now forced into another V litre flask at the same temperature, then

$$P = P_A + P_B + P_C \qquad \qquad \cdots \text{ (i)}$$

where, P is the the total pressure of the gaseous mixture.

Now, $$P_A = n_A \frac{RT}{V} .$$

$$P_B = n_B \frac{RT}{V} \text{ and } P_C = n_C \frac{RT}{V} .$$

$$\therefore \quad P = n_A \frac{RT}{V} + n_B \frac{RT}{V} + n_C \frac{RT}{V}$$

$$= (n_A + n_B + n_C) \frac{RT}{V} = n \frac{RT}{V}$$

where $\qquad n = (n_A + n_B + n_C)$.

$$\therefore \qquad \frac{RT}{V} = \frac{P}{n}$$

Thus, $P_A = \left(\frac{n_A}{n}\right) P$, $\quad P_B = \left(\frac{n_B}{n}\right) P$ and $P_C = \left(\frac{n_C}{n}\right) P$.

7. Graham's Law of Gaseous Diffusion : Two or more gases, which do not react chemically, when brought in direct contact, they have a natural tendency to get mixed up with one another. This tendency of gases is known as **diffusion**. Regarding the diffusion of various gases, Graham propounded a law which is stated as,

Under the similar conditions of pressure and temperature, the rates of diffusion of two gases are inversely proportional to the square root of their densities or the molecular masses.

Let D_A and D_B be the densities of two gases A and B, and M_A and M_B be their molecular masses respectively. Then, according to Graham's Law, we have

$$\frac{r_A}{r_B} = \sqrt{\frac{D_B}{D_A}} = \sqrt{\frac{2D_B}{2D_A}} = \sqrt{\frac{M_B}{M_A}}$$

where r_A and r_B are the rates of diffusion of A and B respectively.

Thus, the gases with high molecular mass will diffuse slowly, and the gases with low molecular weight will diffuse rapidly. In other words, the heavier gases will diffuse slowly and lighter gases will diffuse rapidly.

Rate of diffusion : The volume of a gas diffusing through a porous pot per unit time is known as the rate of diffusion of the gas.

Let V litre be the volume diffused in t second. Then,

$$\text{rate of diffusion} = \frac{V}{t} \text{ litre sec}^{-1}.$$

Experiment to demonstrate that lighter gases diffuse faster than the heavier gases :

The outline of the apparatus used is drawn in the fig. given on page 172. The porous pot A contains air. A jar B, filled
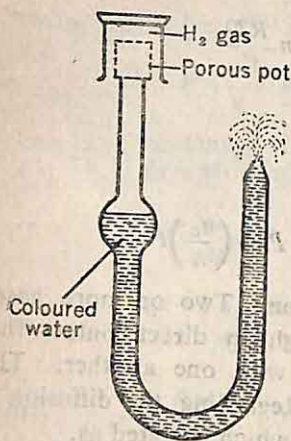
with the hydrogen gas, is inverted over the porous pot. A U-tube connected to the porous pot is filled with some coloured water. It is found that the level of coloured water in the U-tube starts moving up. After some time, a fountain of coloured water is seen coming out through the jet of the U-tube.

Hydrogen is lighter than air. So, it diffuses into the porous pot more rapidly. Air being a heavier gas diffuses out of the porous pot slowly. Thus, in a given time, more hydrogen enters the porous pot than the air coming out of it. The pressure of the gas inside the porous pot, thus, increases and hence the level of coloured water in the U-tube starts rising.

If hydrogen gas is replaced by carbon dioxide, which is heavier than air, it is found that the level of coloured water in the U-tube starts receding. This is because air diffuses out of the porous pot more rapidly than carbon dioxide diffusing into the pot.

The Kinetic Theory of Gases : The kinetic theory of gas first proposed by Bernoulli (1738) and latter developed by Clausius, Maxwell and Boltzmann gives a theoretical explanation of the properties of ideal gases. The theory is based on the following assumptions—

(i) Every gas is composed of a large number of exceedingly small particles, called molecules. All the molecules of a particular gas are identical.

(ii) The molecules of a gas contained in a vessel are in a state of constant chaotic motion in all possible directions. They move in straight lines. Collisions with each other and the walls of the containing vessel cause a change in the direction of motion.

(iii) The collisions between the molecules are perfectly elastic, and hence, there is no loss of kinetic energy or momentum on impact.

(iv) There is no attractive forces between the molecules, and so the molecules move quite independently of each other.

(v) The actual volume of the molecules is negligible compared to the total volume occupied by the gas.

(vi) The pressure exerted by a gas is due to the collisions of molecules with the walls of the containing vessel.

(vii) The absolute temperature of a gas is a measure of average kinetic energy of all the molecules of the gas and is directly proportional to it.

(viii) The effect of gravity on the motion of molecules in a gas is negligible.

Normal Temperature and Pressure (N.T.P.) : The standard values universally accepted are 0°C (or 273 K) and the pressure of the atmosphere equal to 760 mm of mercury-column. These standard conditions are referred to as **Normal Temperature and Pressure** (N.T.P.).

Solved Numerical Problems

Problems based on Boyle's and Charles' Laws :

1. Calculate the number of moles of hydrogen present in 18 litres of gas at a pressure of 70 cm of mercury and at 27°C temperature.

Solution : $$PV = nRT$$

$$\therefore \qquad n = \frac{PV}{RT}$$

Here, $P = \frac{70}{76}$ atmosphere.
$V = 18$ litres
$T = 273 + 27 = 300$ K.
$R = 0.082$ litre atmosphere.

$$\therefore \qquad n = \frac{PV}{RT} = \frac{70 \times 18}{76 \times 0.082 \times 300} = 0.674 \text{ moles.}$$

2. The volume of a gas is 200 ml under a pressure of 2 atmospheres. How many atmospheres of pressure must be applied to reduce the volume to 50 ml, at the same temperature ?

Solution : Initial volume $= 200$ ml $= V_1$
Initial pressure $= 2$ atm. $= P_1$
Final volume $= 50$ ml $= V_2$.

Let the final atmospheric pressure be P_2.
Then, $\because$ $P_1 V_1 = P_2 V_2$ (T being the same)
$\therefore$ $2 \times 200 = P_2 \times 50$

or $$P_2 = \frac{2 \times 200}{50} = 8 \text{ atmospheres.}$$

3. Calculate the density of ammonia at a temperature of 30°C and 5 atmospheric pressure. (I.I.T 1978)

Solution : Volume of 1 mole of ammonia at N.T.P. $= 22.4$ litres.
Suppose, the volume of ammonia at 30°C (or 303 K) and 5 atm. pressure is V_2.

According to the Gas Law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or $\dfrac{1 \times 22 \cdot 4}{273} = \dfrac{5 \times V_2}{303}$

or $V_2 = \dfrac{1 \times 22 \cdot 4 \times 303}{273 \times 5} = 4 \cdot 97$ litres

$\therefore$ Density of ammonia $= \dfrac{\text{Molecular mass}}{\text{Volume of 1 mole}}$

          $= \dfrac{17}{4 \cdot 97} = 3 \cdot 42$ g/litre.

4. The pressure of a gas is 2·5 atmospheres at 27°C. Mass and volume of the gas remaining constant, calculate its temperature when pressure becomes 2·6 atmospheres.

Solution : $P_1 = 2 \cdot 5$ atmospheres,
        $T_1 = 273 + 27 = 300$ K,
        $P_2 = 2 \cdot 6$ atmospheres,
        $T_2 = ?$

$\therefore$ $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2},$ $\therefore$ $V_1 = V_2$

$\therefore$ $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2};$ or $\dfrac{2 \cdot 5}{300} = \dfrac{2 \cdot 6}{T_2}$

or $T_2 = \dfrac{2 \cdot 6 \times 300}{2 \cdot 5} = 312$ K.

$\therefore$ Temperature in centigrade $= 312 - 273 = 39°$C.

5. The density of Oxygen is 16 and that of Nitrogen 14 at 0°C and 760 mm pressure. At what temperature will Oxygen have the same density as Nitrogen at 0°C, assuming that the pressure remains constant ?

Solution : The density of the gas varies inversely as the absolute temperature.

The density of Oxygen at 0°C or 273 K = 16.

Let the temperature at which the density of Oxygen will become 14 be T.

$\therefore$ $\dfrac{16}{14} = \dfrac{T}{273}$

or $T = \dfrac{16 \times 273}{14} = 312$ K $= (312 - 273)°$C $= 39°$C.

6. Calculate the volume of one mole of Oxygen at 27°C and 2

atmospheric pressure. Molar volume of Oxygen at N. T. P. is
22·4 litres.   **(I. I. T. Entrance Exam.)**

Solution : The volume of 1 mole of O_2 at N. T. P. = 22·4 litres.

$$\text{Normal temp.} = 0°C = 273 \text{ K}$$
$$\text{Normal pressure} = 760 \text{ mm.}$$

Let the required volume be V litre.

$$\therefore \quad \frac{2 \times V}{(273 + 27)} = \frac{1 \times 22·4}{273}$$

or $\qquad V = \frac{22·4 \times 300}{2 \times 273} = 12·3$ litres.

7. Air weighs 1·29 g/litre at standard conditions. Calculate the
density of air at a place where the pressure is 450 mm Hg and the
temperature 17°C.

Solution : Volume of air = 1 litre

$$\text{Temperature} = 0°C = 273 \text{ K}$$
$$\text{Pressure} = 760 \text{ mm.}$$

Let us calculate the volume at 17°C (or 290 K) and 450 mm
pressure. According to the gas equation,

$$\frac{760 \times 1}{273} = \frac{V \times 450}{290}$$

or $\qquad V = \frac{290 \times 760}{273 \times 450}$ litre = 1·794 litre.

Now, $\because$ weight of 1·794 litre air is 1·29 g,

$\therefore$ weight of 1 litre air is $\frac{1·29}{1·794}$ g = 0·719 g

i.e. required density = 0·719 g/litre.

8. What weight of Nitrogen at 10°C and 566 mm pressure shall
occupy a volume of 380 ml ?

Solution : Volume of Nitrogen = 380 ml

$$\text{Temperature} = 10°C = (273 + 10) \text{ K} = 283 \text{ K}$$
$$\text{Pressure} = 566 \text{ mm.}$$

Let the volume of the gas at N. T. P. be V ml.

$$\therefore \quad \frac{760 \times V}{273} = \frac{566 \times 380}{283}$$

or $\qquad V = \frac{566 \times 380 \times 273}{760 \times 283} = 273$ ml = 0·273 litre.

$\because$ 22·4 litres of N_2 at N. T. P. weigh 28 g,

$\therefore$ 0·273 ,,   ,,   ,,   ,, $\frac{28 \times 0·273}{22·4}$ g = 0·3412 g.

9. 2·70 litres of a gas weighed 1·518 g at 87°C and 0·6 atmosphere pressure. Calculate the molecular weight of the gas.

Solution : Volume of the gas = 2·70 litres, Temp. = 87°C = 360 K

$$\text{Pressure} = 0·6 \text{ atmosphere.}$$

Let the volume at N. T. P. be V litre. Then

$$\frac{2·7 \times 0·6}{360} = \frac{V \times 1}{273}$$

or $$V = \frac{2·7 \times 0·6 \times 273}{360} = 1·2285 \text{ litre.}$$

∵ 1·2285 litre of gas at N. T. P weigh 1·518 g,

∴ 22·4 litres ,, ,, ,, $\dfrac{22·4 \times 1·518}{1·2285}$ g

$$= 27·67 \text{ g.}$$

10. An open vessel is heated at 27°C till $\frac{2}{5}$ part of its air is expelled. If the volume of the vessel remains constant, calculate the temperature to which the vessel has been heated. **(I. I. T. 1977)**

Solution : As the vessel is open, pressure will remain constant. Volume also is constant.

Now, $$PV = n_1 RT_1 \text{ and } PV = n_2 RT_2$$

∴ $$n_1 RT_1 = n_2 RT_2; \quad \text{or} \quad \frac{n_1}{n_2} = \frac{T_2}{T_1}.$$

Let n_1 be equal to 1. Hence, $n_2 = 1 - \frac{3}{5} = \frac{2}{5}$

∴ $$\frac{1 \times 5}{2} = \frac{T_2}{(273+27)}; \quad \text{or} \quad \frac{5}{2} = \frac{T_2}{300}$$

or $$T_2 = \frac{5 \times 300}{2} = 750 \text{ K} = 750 - 273 = 477°C.$$

11. At what temperature will a given volume of a gas at 0°C double itself, pressure remaining constant ?

Solution : Let the volume of the gas be V ml.

Initial temperature of the gas = 0°C = 273 K.

Let the temperature at which the volume is doubled be T K. As pressure is constant,

$$\frac{V}{273} = \frac{2V}{T}$$

or $$T = 2 \times 273 = 546 \text{ K} = 546 - 273 = 273°C.$$

Problems based on Dalton's Law of partial pressure :

12. The total pressure exerted by a mixture of two gases A and B is 76·2 cm. The number of moles of the two gases are 0·0075 and 0·0040 respectively. Calculate the partial pressures of the two gases.

Solution : $n_A = 0·0075$, and $n_B = 0·0040$

$\therefore$ $n = n_A + n_B = 0·0075 + 0·0040 = 0·0115$

Now, partial pressure of A, $P_A = \left(\dfrac{n_A}{n}\right) P$

$$= \frac{0·0075}{0·0115} \times 76·2 = 49·7 \text{ cm of Hg}$$

$\therefore$ Partial pressure of B, $P_B = P - P_A$
$$= 76·2 - 49·7 = 26·5 \text{ cm of Hg.}$$

Problems based on Graham's Law of diffusion :

13. The rates of diffusion of carbon dioxide and ozone are 0·29 and 0·274 respectively. The relative density of carbon dioxide is 22 ($H = 1$). What is the relative density of ozone ?   (M. U. 1978A)

Solution : From Graham's law, we have,

$$\frac{r_1}{r_2} = \sqrt{\frac{D_2}{D_1}}$$

By the question, $r_1 = 0·29$, $r_2 = 0·274$
$$D_1 = 22, \; D_2 = ?$$

$\therefore$ $\dfrac{0·29}{0·274} = \sqrt{\dfrac{D_2}{22}}$;   or $\dfrac{0·29 \times 0·29}{0·274 \times 0·274} = \dfrac{D_2}{22}$

or, $D_2 = \dfrac{0·29 \times 0·29 \times 22}{0·274 \times 0·274} = 24·6$.

14. In an experiment, it was found that 500 ml of a gas A diffused through a hole into a vacuum in the same time as 620 ml of air. Calculate the density of A relative to air.

Solution : According to Graham's law,

$$\sqrt{\frac{\text{Density of } A}{\text{Density of air}}} = \frac{\text{Rate of diffusion of air } (r_1)}{\text{Rate of diffusion of } A \; (r_2)}$$

$$\frac{r_1}{r_2} = \frac{620/t}{500/t} \qquad (t = \text{time})$$

INTR. CH.-12

$$\therefore \quad \sqrt{\frac{\text{Density of } A}{\text{Density of air}}} = \frac{620}{500}$$

or,

$$\frac{\text{Density of } A}{\text{Density of air}} = \frac{620 \times 620}{500 \times 500} = 1 \cdot 54$$

$$\therefore \quad \text{Density of } A \text{ relative to air} = 1 \cdot 54$$

15. A straight glass tube has two holes X and Y at its two ends. The tube is 200 cm long. HCl and NH_3 gases are allowed to pass through the tube simultaneously through X and Y respectively. White fumes appeares at point P inside the tube. Find the distance between P and X.   (I. I. T. 1980)

Solution :
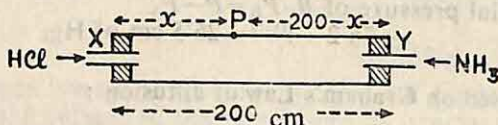
Molecular mass of $HCl = 1 + 35 \cdot 5 = 36 \cdot 5$
Molecular mass of $NH_3 = 14 + 3 \times 1 = 17$

$$\frac{\text{Rate of diffusion of } HCl}{\text{Rate of diffusion of } NH_3} = \sqrt{\frac{17}{36 \cdot 5}}$$

Let the distance between P and X be x. Hence, the distance between P and $Y = (200 - x)$ cm.

$$\therefore \quad \frac{\text{Rate of diffusion of } HCl}{\text{Rate of diffusion of } NH_3} = \frac{x}{200 - x}$$

$$\therefore \quad \frac{x}{200 - x} = \sqrt{\frac{17}{36 \cdot 5}} = 0 \cdot 6824$$

or $\quad x = 0 \cdot 6824 (200 - x);$ or $\quad x + 0 \cdot 6824 x = 0 \cdot 6824 \times 200$

or $\quad 1 \cdot 6824 x = 136 \cdot 48;$ or $\quad x = \dfrac{136 \cdot 48}{1 \cdot 6824} = 81 \cdot 12$ cm.

16. One litre each of Nitrogen and Hydrogen weigh 1·25 g. and 0·09 g respectively. Calculate the volume of Nitrogen which would diffuse through a porous membrane of 3 square centimetres in area in the same time as 100 ml of Hydrogen.

Solution : 1 litre of N_2 weighs 1·25 g.
$\therefore$ 22·4 litre of N_2 will weigh $1 \cdot 25 \times 22 \cdot 4$ g $= 28$ g
$\therefore$ Molecular weight of Nitrogen $= 28$.
Similarly, 1 litre of H_2 weighs 0·09 g.
$\therefore$ 22·4 litre of H_2 will weigh $0 \cdot 09 \times 22 \cdot 4$ g $= 2$ g.

$\therefore$ Molecular weight of Hydrogen $= 2$
    Volume of Hydrogen diffused $= 100$ ml
Let the time required for diffusion of H_2 be t sec.

$\therefore$ Rate of diffusion, $r_1 = \dfrac{100}{t}$

Let the volume of Nitrogen that diffuses in the same time be V_i ml.

$\therefore$ Rate of diffusion, $r_2 = V/t$.

$\therefore$ $\dfrac{r_1}{r_2} = \dfrac{100/t}{V/t} = \dfrac{100}{V}$;   But $\dfrac{r_1}{r_2} \sqrt{\dfrac{28}{2}}$

$\therefore$ $\dfrac{100}{V} = \sqrt{\dfrac{28}{2}}$;   or, $\dfrac{100 \times 100}{V^2} = \dfrac{28}{2}$

or $V^2 = \dfrac{2 \times 100 \times 100}{28}$;   or $V = \sqrt{\dfrac{10000}{14}}$

$\therefore$ $= 26 \cdot 83$ ml.

Questions

Long Answers Type :

1. State two characteristics of a gaseous state.
2. What do you mean by the equation of state of a gas ?
3. State and explain Dalton's law of partial pressure.
4. What is gaseous diffusion ?   Describe a simple experiment to show gaseous diffusion.   (R.U. 1973A)
5. 'Lighter gases diffuse more rapidly than heavier gases. Give an experimental support for this.   (Mith.U. 1978A)
6. Deduce an expression combining Boyle's and Charles' laws.
7. Discuss the usefulness of Avogadro's hypothesis.
8. What are the main assumptions of the kinetic theory of gases ?

Short Answer Type :

1. Enunciate Boyle's law.
2. State Charles' law.
3. State Graham's law of gaseous diffusion.
4. What is the rate of diffusion ?
5. State Avogadro's hypothesis.
6. If the temperature of a gas in centigrade is doubled, will its volume be also doubled ? If not, prove.

[Ans. : Volume will not be doubled, because volume is proportional to absolute temperature but not proportional to temperature on centigrade scale.

Objective Type :

(A) Four answers are given to each question below but, only one of them is correct. Assign mark '$\sqrt{}$' to the correct answers :

15. Boyle's law says that if P is the pressure, T is the temperature and V the volume then,

    (a) $\dfrac{P_1}{P_2} = \dfrac{V_2}{V_1}$ at constant temperature,

    (b) $\dfrac{P_1}{P_2} = \dfrac{V_1}{V_2}$ at constant T.

    (c) $\dfrac{V_1}{V_2} = \dfrac{T_1}{T_2}$ at constant P.

    (d) $\dfrac{P_1}{P_2} = \dfrac{V_2}{V_1}$ at constant T and mass of gas.

16. The molar gas constant R, equals to
    (a) 22·41 litres,   (b) 0·0821 lit. atm/deg.,
    (c) 831·42 cal/deg.,   (d) 1·987 joules/deg.

17. 10 g each of hydrogen, oxygen and nitrogen are taken separately in three vessels. The order of decreasing number of molecules is :
    (a) nitrogen, hydrogen, oxygen. (b) hydrogen, nitrogen, oxygen.
    (c) hydrogen, oxygen, nitrogen. (d) oxygen, nitrogen, hydrogen.

18. The rate of diffusion of a gas is inversely proportional to the square root of its density. Two balloons are filled up with H_2 and O_2 separately at the same temperature and pressure. If oxygen diffuses at the rate of 65 ml per hour, hydrogen will diffuse at the rate of
    (a) 64 ml per hour,   (b) 66 ml per hour,
    (c) 4 ml per hour,   (d) 260 ml per hour.

19. If the pressure and absolute temperature of 2 litres of CO_2 are doubled, the volume of CO_2 would become
    (a) 2 litres,   (b) 1 litre,   (c) 4 litres,   (d) 8 litres.

20. The volume of a given mass of gas is 117 ml at 39°C. At what temperature will it be 213 ml ?
    (a) 273 k,   (b) 39°C,   (c) 426 k,   (d) 143 k,
    (e) −71°C.   **(PMDT 1975)**

21. Two litres of a gas are maintained at 250°C and 2 atmospheres. If pressure is doubled and absolute temp. is halved, the gas will now occupy
    (a) 4 litres,   (b) 2 litres,   (c) 1 litre,   (d) 0·5 litre.

22. What will be the density of a gas (mole wt.=44·8) in gm/litre at 273°C and 1 atm. pressure ?
    (a) 8·6,   (b) 11·2,   (c) 1,   (d) 2,   (e) 4.

23. 300 ml of the gas are heated from 27°C to 127°C. What will be the new volume of the gas at constant pressure ?
    (a) 400 ml,   (b) 225 ml,   (c) 300 ml,   (d) 600 ml.

24. The rate of diffusion of H_2 and Cl_2 are in the ratio of 1·6. The density of Cl_2 as compared to that of H_2 will be
    (a) 72,   (b) 36,   (c) 18,   (d) 6,   (e) 26.

25. The density and rate of diffusion of a gas A are D and R respectively. The corresponding values of another gas B are d and r. When D/d is equal to 4, R/r is equal to
    (a) $\frac{1}{2}$.   (b) $\frac{1}{4}$,   (c) 2,   (d) 4.

26. The rates of diffusion of hydrogen and deuterium are

(a) 1 : 2,   (b) 1 : $\sqrt{2}$,   (c) $\sqrt{2}$: 1,   (d) 4 : 1.

27. A gas A diffuses three times as fast as another gas B. The ratio of the densities of A and B is

(a) 1 : 3,   (b) 3 : 1,   (c) 9 : 1,   (d) 1 : 9.

28. The partial pressure of H_2 in a flask containing 2·016 g of H_2 and 16·00 g of O_2 is

(a) $\frac{1}{8}$th total pressure,   (b) $\frac{1}{8}$th the total pressure,
(c) $\frac{1}{4}$th the total pressure,   (d) $\frac{2}{3}$rd the total pressure.

Numerical Problems :

1. The volume of a gas is 910 ml at 0°C and 760 mm. pressure. What will be the volume of the gas when the temperature becomes 27°C and pressure 728 mm ?
(Ans. 1043·95 ml)

2. Calculate the temperature at which air possesses a density equal to that of hydrogen at 0°C. (Density of air = 14·4)
(Ans. 3658·2°C)

3. What is the effect of doubling the pressure and doubling the absolute temperature on the volume of a gas ?

4. A gas has a density of 1·85 g/litre at 25°C and 700 mm pressure. What is its molecular weight ?

5. 10 ml of Hydrogen was measured at 20°C. What will be the volume at 100°C, the pressure being constant ?
(Ans. 12·37 ml)

6. At what temperature would the volume of a gas be doubled, if the pressure at the same time increases from 700 to 800 mm. ?
(Ans. 351°C)

7. 400 ml of oxygen are collected over water at 17°C and 750 mm pressure. What will be the volume of the dry gas at N.T.P. ? (Aqueous tension at 17°C = 14·4 mm)

[Solution : Pressure of oxygen = (750 − 14·4)mm = 735·6 mm.
Let the volume at N.T.P. be V ml.

$$\therefore \ \frac{760 \times V}{273} = \frac{735·6 \times 400}{(273+17)} \ ; \quad \text{or,} \quad \frac{760 \times V}{273} = \frac{735·6 \times 400}{290}$$

$$\text{or,} \quad V = \frac{735·6 \times 400 \times 273}{760 \times 290} = 364·46 \text{ ml}]$$

8. What is the density of Carbon dioxide at 100°C and 720 mm. ?

[Hint :   Volume of 1 mole = $\frac{22·4 \times 760 \times 373}{720 \times 273} = 32·3$ litre

$$\therefore \quad \text{Density} = \frac{44 \text{ g}}{32·3 \text{ litre}} = 1·36 \text{ g litre}^{-1}.]$$

Based on Dalton's law of partial pressure :

9. A 10 litre flask at 298 k contains a gaseous mixture of carbon monoxide and carbon dioxide at a total pressure of 2·0 atmospheres. If 0·20 mole of carbon monoxide is present find out its partial pressure and also that of carbon dioxide.
(Ans. $P_{CO_2} = 1·51$ atm; $P_{CO} = 0·49$ atm)

10. Two volumes of oxygen and two volumes of chlorine are mixed together. What will be the partial pressure of each when the barometre stands at 760 mm. ?

(Ans. $O_2 = 456$ mm.; $Cl_2 = 304$ mm.)

Diffusion of gases :

11. Hydrogen sulphide (H_2S) and chlorine (Cl_2) have distinct but different odours. If equal quantities of the two gases are simultaneously released in one corner of the laboratory under exactly similar conditions, which gas will be detected first by students on the far side of the laboratory ?   Give reasons for your answer.

12. Pure oxygen effuses through an aperture in 224 second whereas mixture of ozone and oxygen, containing 20% by volume of ozone, effused from the same effusiometer in 234 sec. What is the molecular weight of ozone ? **(Ans.** 46·5)

13. The gases SO_2 and H_2S, are admitted at opposite ends of a 100 cm. tube, the tube is sealed, and the gases diffuse towards each other.   At what point will free sulphur, the product of their chemical interaction, first appear ?

(Ans. 42·2 cm. from SO_2 end of the tube)

CHATPER 9

MOLE CONCEPT

Need for Mole Concept—The need for mole concept arises on account of the following grounds :

(i) The basic unit of a chemical substance is an atom or a molecule is necessary. While working in the laboratory, we have to use a definite number of atoms or molecules of any substance. For example, suppose two substances A and B react in such a way that one atom of A combines with one atom of B. In the laboratory, it will be required to use as much amounts of A and B as would provide equal number of atoms of A and B. This would ensure that the whole amount of A will be consumed in reaction with the whole amount of B. It is here that the mole concept comes to our help.

(ii) A mole is an unit for counting atoms, molecules or ions. A mole is a collection of 6.023×10^{23} atoms, molecules or ions.

(iii) The masses of the atoms and molecules are exceedingly small. Even a very small amount of a substance contains a very large number of atoms or molecules. It has been found that 1 mg of carbon contains 5019×10^{16} atoms. This figure being very big is not convenient for our use in calculations. Hence, a collection of 6.023×10^{23} atoms, molecules or ions is called a **mole**.

1 mole of atoms $= 6.023 \times 10^{23}$ atoms.
1 mole of molecules $= 6.023 \times 10^{23}$ molecules.

Atomic Mass Unit (a.m.u.) : The mass of a C^{12} atom has been assigned the value of 12.0000. Atomic masses of all other elements are then based on this reference. For example, if atoms of an element have an average mass twice that of C^{12}, the element is assigned an atomic mass of 24.

The mass of a C^{12} atom divided by 12 is known as the **atomic mass unit**. The atomic mass of an element may now be defined as :

The atomic mass of an element is a number which shows how many times the atom of the element is heavier than one-twelveth the mass of a C^{12} atom.

The atomic masses of some common elements are given in the table below.

Element	Symbol	Atomic number	Atomic mass (a.m.u.)
Hydrogen	H	1	1·008
Helium	He	2	4·003
Lithium	Li	3	6·940
Beryllium	Be	4	9·013
Boron	B	5	10·82
Carbon	C	6	12·01115
Nitrogen	N	7	14 0067
Oxygen	O	8	15·9994
Fluorine	F	9	19·00
Neon	Ne	10	20·183
Sodium	Na	11	22·9898
Magnesium	Mg	12	24·32
Aluminium	Al	13	26·97
Silicon	Si	14	28·09
Phosphorus	P	15	30·98
Sulphur	S	16	32·064
Chlorine	Cl	17	35·453
Argon	A	18	39·944
Potassium	K	19	39·09
Calcium	Ca	20	40·08
Manganese	Mn	25	54·94
Iron	Fe	26	55·847
Copper	Cu	29	63·546
Zinc	Zn	30	65·38
Bromine	Br	35	79·916
Silver	Ag	47	107·880
Tin	Sn	50	118·70
Iodine	I	53	126·9045
Barium	Br	56	137·34
Gold	Au	79	196·9665
Lead	Pb	82	207·21

Gram-atom or Gram-atomic mass—When the atomic mass of an element is expressed in gram, it is called a gram-atom. For example, the atomic mass of oxygen is 15·9994. Hence, 15·9994 gram oxygen = 1 gram-atom oxygen.

i.e., $$\text{Gram-atom} = \frac{\text{Mass of the element in gram}}{\text{Atomic mass of the element}}$$

1 gram-atom of an element = Atomic mass of the element expressed in gm = Mass of $6·023 \times 10^{23}$ atoms.

Molecular mass—The mass of a molecule of a substance, expressed in a.m.u., is called the molecular mass of the substance. It may be defined as :

The molecular mass of a substance is a number which indicates how many times a molecule of the substance is heavier than one-twelveth the mass of a C^{12} atom.

i.e.;   Molecular mass $= \dfrac{\text{Mass of one molecule of the substance}}{\frac{1}{12} \text{ the mass of } C^{12} \text{ atom}}$

The molecular mass is obtained by adding up the atomic masses of all atoms present in a molecule of the substance.

(i) Molecular mass of Water $(H_2O) = 2 \times 1 \cdot 008 + 1 \times 15 \cdot 9994$
$$= 18 \cdot 0154 \text{ a.m.u.}$$

(ii) Molecular mass of Sulphuric acid (H_2SO_4)
$$= 2 \times 1 \cdot 008 + 32 \cdot 064 + 4 \times 15 \cdot 9994 = 98 \cdot 0776 \text{ a.m.u.}$$

Gram-mole or Gram-molecular Mass—The molecular mass of a substance, when expressed in gram, is known as the gram-mole. For example, the molecular mass of sulphuric acid is $98 \cdot 0776$ a.m.u. Hence, $98 \cdot 0776$ gram sulphuric acid is 1 gram-mole sulphuric acid.

i.e.,   Gram-mole $= \dfrac{\text{Mass of the substance in gram}}{\text{Molecular mass of the substance}}$

Gram-molecular Volume—The volume occupied by a gram-mole of any gas at N.T.P. is $22 \cdot 4$ litre, and this volume is known as the gram-molecular volume. This volume of gas contains

$$6 \cdot 023 \times 10^{23} \text{ molecules.}$$

Mole—A collection of $6 \cdot 023 \times 10^{23}$ atoms, molecules or ions is called a mole.

i.e.,   1 mole $= 6 \cdot 023 \times 10^{23}$ atoms, molecules or ions.

The mole is a concept of quantity in terms of a number of particles, and hence represents a certain mass. In general, the term mole represents a gram-atom, a gram-mole or a gram-ion.

i.e.,   1 Mole $=$ Avogadro's number of particles.
$$= 6 \cdot 023 \times 10^{23} \text{ particles.}$$

Avogadro's number (N) : Avogadro's number is usually defined as the number of atoms present in one gram-atom of an element or the number of molecules present in one gram-mole of a substance (element or compound) or the number of ions present in one gram-ion of a substance.

i.e.,

$$N = 6 \cdot 023 \times 10^{23}$$

Numerical Problems

1. Calculate the number of moles in each of the following amounts of material :

(a) $10 \cdot 00$ g of H_2SO_4.
(b) $1 \cdot 00$ molecule of NO_2.

Solution : (a) Molecular mass of $H_2SO_4 = 98 \cdot 0776$ a.m.u.

∴   Moles of $H_2SO_4 = \dfrac{\text{Weight of } H_2SO_4}{\text{Molecular mass}} = \dfrac{10 \cdot 00}{98 \cdot 0776}$

(b) $\because$ $6 \cdot 023 \times 10^{23}$ molecules of $NO_2 = 1$ mole,

$$\therefore 1 \cdot 00 \qquad " \qquad = \frac{1}{6 \cdot 023 \times 10^{23}} \text{mole}$$

$$= \frac{1}{6 \cdot 023} \times 10^{-23} \text{ mole.}$$

2. Calculate the number of H_2O molecules in one litre of water. Calculate the mass of a single molecule of water. (Assume the density of water to be 1 g/ml).

Solution : 1 litre of water = 1000 ml of water
= 1000 g of water.

$$\text{Mole of water} = \frac{\text{Weight of water}}{\text{Molecular mass of water}} = \frac{1000}{18 \cdot 0154}$$

$\because$ 1 mole contains $6 \cdot 023 \times 10^{23}$ water molecules,

$$\therefore \frac{1000}{18 \cdot 0154} \quad " \quad \frac{6 \cdot 023 \times 10^{23} \times 1000}{18 \cdot 0154} \text{ water molecules.}$$

$$= 3 \cdot 344 \times 10^{25} \text{ molecules litre}^{-1}$$

Now, $\because$ $3 \cdot 344 \times 10^{25}$ molecules weight 1000 gm

$$\therefore 1 \qquad " \qquad \frac{1000}{3 \cdot 44 \times 10^{25}} \text{ g}$$

$$= 2 \cdot 990 \times 10^{-23} \text{ g molecule}^{-1}.$$

3. The electrical charge on a single electron is found to be $1 \cdot 6 \times 10^{-19}$ coulombs. Calculate the total charge of a mole of electrons.

Solution : 1 mole of electrons = $6 \cdot 023 \times 10^{23}$ electrons.
$\therefore$ Total charge of a mole of electrons
$= 1 \cdot 6 \times 10^{-19} \times 6 \cdot 023 \times 10^{23}$ coulombs.
$= 9 \cdot 632 \times 10^{4}$ coulomb mole^{-1}.

4. Calculate the number of Na^+ and Cl^- ions in a mole of $NaCl$.

Solution : 1 mole of $NaCl = 22 \cdot 99 + 35 \cdot 45 = 58 \cdot 44$ g
$$NaCl \rightarrow Na^+ + Cl^-$$
1 mole   1 g-ion   1 g-ion
$\therefore$ Number of Na^+ ions = $6 \cdot 023 \times 10^{23}$
Number of Cl^- ions = $6 \cdot 023 \times 10^{23}$
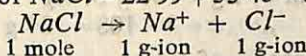
5. Calculate the number of Ba^{++} and Cl^- ions in a mole of $BaCl_2$.
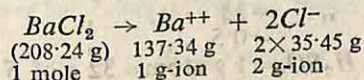
Solution :
$$BaCl_2 \rightarrow Ba^{++} + 2Cl^-$$
(208·24 g)   137·34 g $2 \times 35 \cdot 45$ g
1 mole   1 g-ion   2 g-ion
$\therefore$ Number of Ba^{++} ions = 6 023 $\times 10^{23}$
Number of Cl^- Ions = $2 \times 6 \cdot 023 \times 10^{23}$
$= 12 \cdot 046 \times 10^{23} = 1 \cdot 2046 \times 10^{24}$.

6. Calculate the number of atoms in a milligram of silver.

Solution : 1 mg silver $= 0{\cdot}001$ g silver

$$= \frac{0{\cdot}001}{107{\cdot}87} \text{ mole } Ag \text{ (Atomic mass of } Ag$$
$$= 107{\cdot}87)$$

$\because$ 1 mole Ag contains $6{\cdot}023 + 10^{23}$ atoms,

$\therefore$ $\dfrac{0{\cdot}001}{107{\cdot}87}$ mole Ag ,, $\dfrac{6{\cdot}023 \times 10^{23} \times 0{\cdot}001}{107{\cdot}87}$ atoms

$$= 5{\cdot}58 \times 10^{18} \text{ atoms.}$$

7. From 200 mg of CO_2, 10^{21} molecules are removed. How many moles of CO_2 are left ?   **(I. I. T. 1978)**

Solution : 1 mole $= 6 \times 10^{23}$ molecules.
                $= 1$ gm-mole.

200 mg of CO_2 (mole. wt. $= 44$) $= \dfrac{200 \times 10^{-3}}{44}$ mole

$$= 4{\cdot}55 \times 10^{-3} \text{ mole}$$

Molecules removed $= 10^{21} = \dfrac{10^{21}}{6 \times 10^{23}} = 1{\cdot}67 \times 10^{-3}$ moles

$\therefore$ Moles of CO_2 left $= (4{\cdot}55 \times 10^{-3} - 1{\cdot}67 \times 10^{-3})$
                        $= 2{\cdot}88 \times 10^{-3}$ mole.

8. Find the number of gm-atom in 2×10^{23} atoms of an element.

Solution : 1 gm-atom of an element $= 6{\cdot}023 \times 10^{23}$ atoms.
Now, $\because$ $6{\cdot}023 \times 10^{23}$ atoms $= 1$ gm-atom

$\therefore$ 2×10^{23} atom $= \dfrac{2 \times 10^{23} \times 1}{6{\cdot}023 \times 10^{23}} = \dfrac{1}{3{\cdot}0115}$ gm-atom.

9. How many grams are present in 3 gm-atoms of Ag ?
                            (At. wt. of $Ag = 108$)

Solution : 1 gm-atom of $Ag = 108$ g of Ag
$\therefore$ 3   ,,   ,, $= 3 \times 108 = 324$ g of Ag.

10. How many gm-atoms of S are present in 49 g of H_2SO_4 ?

Solution : $H_2SO_4 = 2 + 32 + 64 = 98$
         1 mole of $H_2SO_4 = 98$ g
or,   98 g of $H_2SO_4 = 1$ mole of H_2SO_4
$\therefore$ 49 g   ,, $= \frac{49}{98}$,,   ,,
                       $= 0{\cdot}5$,,   ,,
         1 mole of $H_2SO_4 = 1$ s atom $= 32$ g of S

$\therefore$ $0{\cdot}5$,,   ,, $= \dfrac{32 \times 0{\cdot}5}{1} = 16$ g of S.

Questions

Long Answer Type :

1 What is atomic mass unit ? What was the need for the adoption of this unit ?

2. What do you mean by atomic mass and molecular mass ?

3. How is the molecular mass of a substance calculated ? Give one example.

4. What is a mole ?

5. Explain the terms gram-molecular volume.

6. What do you understand by Avogadro's number ?

Short Answer Type :

1. Define 'atomic mass'.

2. How is the gm-atom of an element related to its mass ?

3. What is the number of atoms in a mole of an element ?

Objective Questions.

(A) *Four answers are given to each question below, but only one of them is correct. Assign mark '√' to the correct answer* :

1. 1 mole $NaCl$ is equivalent to

(a) 5·85g $NaCl$, (b) 23g $NaCl$, (c) 58·5g $NaCl$, (d) 35·5 g $NaCl$.

2. How many gm atoms are present in 4·632 gm of platinum ? (At. wt of $Pt = 195·09$).

(a) 0·24, (b) 2·4, (c) 0·024, (d) 2·24

3. How many platinum atoms are present in 0·4632gm of Pt ? (At. wt. of $Pt = 195·09$).

(a) $1·4 \times 10^{21}$ atoms, (b) $0·14 \times 10^{21}$ atoms, (c) $1·4 \times 10^{23}$ atoms, (d) $1·4 \times 10^{22}$ atoms.

4. A collection of $6·023 \times 10^{23}$ ions is called a

(a) a.m.u, (b) avogram, (c) gm-atom, (d) mole.

5. The atomic mass of silver is 107·87. The number of moles in 215·74g silver will be

(a) 3, (b) $6·023 \times 10^{23}$, (c) 2, (d) 10.

6. 10g of $CaCO_3$ contains

(a) 10 moles of $CaCO_3$, (b) 1gm atom of Ca, (c) 6×10^{23} atomes of Ca, (d) 0·1 gm eq. of $CaCO_3$.

(I. I. T. 1978)

(B) *A number of statements are given below. Select the correct or the most appropriate statements.*

7. One mole of carbon dioxide contains $6·023 \times 10^{23}$ molecules.

8. The molecular mass of a compound, expressed in gram, is known as the mole.

9. The volume occupied by 1 mole of oxygen at N.T.P. is known as the Normal Volume.

10. A molal solution contains one mole of solute in 1000g of solution.

(I. I. T. 1978)

(C) *Fill up the blanks in the following* :

11. The number of atoms present in 12g carbon is.........

12. The atomic mass of aluminium is 26·9315. Hence, a mole of aluminium ions weighs...........g.

13. The weight of a mole of Ca^{++} ions is equal to a.........of calcium.

Numerical Problems :

1. Calculate the number of moles of carbon dioxide in $12·046 \times 10^{23}$ molecules of CO_2.

[Ans. 2]

2. How many moles of aluminium are there in 5·0g of the element ?

(Ans. 1·83)

3. Calculate the number of moles in 100,00 ml of propane at N.T.P.

(Ans. : 4·46)

4. The density of water at room temperature is 1·0 g/ml. Calculate the number of H_2O molecules in 10 drops of water, when the volume of this much water is 0·5 ml.

(Ans. $1·67 \times 10^{22}$)

5. To a sample of an element X(at. wt.$=70$) another element Y (at. wt.$=120$) is to be added as an impurity. The ratio of atoms in the mixture is to be $1·10^{-4}$. How many grams of Y will be required for 35 grams of X ?

[Solution : (i) Number of atoms in 35g. of X

$$= \frac{35}{70} \times N = 0·5N \ (N = \text{Avogadro's number})$$

(ii) Suppose, $x = 1$ atom and $y = 10^{-7}$ atoms

$\because \ x = 0·5 \ N$ atoms, $\therefore \ y = (0·5N) \times 10^{-7}$ atoms

(iii) $0·5N \times 10^{-7}$ atoms of $Y = 0·5 \times 10^{-7} \times$ gm atom $= 0·5 \times 10^{-7} \times 120$ g.

$= 6·0 \times 10^{-6}$ g.]

6. Determine the number of molecules, and the number of atoms in each of the following quantities.

(a) one mole of H_2O, (b) 5 moles of HCl.
(c) 10_g of CO_2, (d) 100_g of H_2O.

7. How many moles of CaO are present in 60 g of $CaCO_3$?   (Ans. 0·6 mole)

8. Find moles of a gas in 5·6 litres of the gas at N.T.P.   (Ans. 0·25 mole)

9. How many grams of S are required to produce 100 moles of H_2SO_4 ?

(Ans. 3200 g)

10. Determine the number of molecules in 76·9 g of Phosphorus (P_4). $(p=31)$.

(Ans. $3·734 \times 10^{23}$)

□ □ □

ACIDIMETRY AND ALKALIMETRY

Neutralisation—By the term **'neutrlisation'** it is generally meant the combination of hydrogen atoms present in the acid with the oxygen or hydroxyl group present in the base, to produce salt and water.

$$HCl + NaOH \rightarrow NaCl + H_2O$$
(acid)   (base)   (salt)   (water)

$$H_2SO_4 + CuO \rightarrow CuSO_4 + H_2O$$
(acid)   (base)   (salt)   (water)
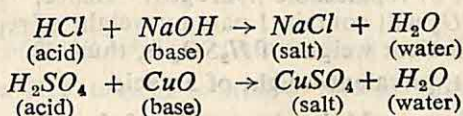
According to the ionic theory, **neutralisation is the process in which H^+ ions of the acid combine with the OH^- ions of the allkali to produce undissociated molecules of water.**

$$H^+ + OH^- \rightarrow H_2O$$
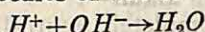
Indicators—Indicators are chemicals used in Volumetric Analysis which indicate, by change of colour, the termination (i.e., end-point) of a chemical reaction.

The indicator also indicates by colour-change whether the solution is acidic, alkaline or neutral.

Some of the indicators which are frequently used in the laboratory are listed below :

Indicator	Colour in solution		
	Alkaline	Neutral	Acidic
Methyl Orange	Yellow	Orange	Pink
Phenolphthalein	Pink	Colourless	Colourless
Litmus	Blue	Violet	Red

Standard Solution—A standard solution is such a solution which contains a known weight of the solute present in a known volume of it.

Titration—The process of determining the strength of an unknown solution by allowing it to react with a solution of known strength, is called Titration.

Acidimetry—The method of determining the strength of an alkali in a solution by neutralising it, in presence of an indicator, with the standard solution of an alkali, is called acidimetry.

Alkalimetry—The method of determining the strength of an acid in a solution by neutralising it, in presence of an indicator, with the standard solution of an alkali, is called alkalimetry.

Equivalent Weight of an acid—It is that weight of an acid which contains one part by weight of replaceable hydrogen.

Example : Hydrochloric acid (HCl)—36·5 parts by weight of HCl contains one part by weight of replaceable hydrogen. Hence, the equivalent weight of $HCl = 36$·5.

Sulphuric acid (H_2SO_4)—98 parts by weight of H_2SO_4 contains 2 parts by weight of replaceable hydrogen. Hence, $\frac{98}{2} = 49$ parts by weight of H_2SO_4 will contain 1 part by weight of replaceable hydrogen. The equivalent weight of H_2SO_4 is, thus, 49.

In general, Equivalent weight of an acid

$$= \frac{\text{Molecular weight of the acid}}{\text{Basicity}}$$

Equivalent weight of an alkali—It is that part by weight of an alkali which will just completely neutralise on equivalent weight of an acid.

Example : (i) $NaOH + HCl \longrightarrow NaCl + H_2O$
$$\begin{array}{cc} 23+16+1 & 1+35·5 \\ =40 & =36·5 \end{array}$$

40 parts by weight of $NaOH$ just completely neutralises 36·5 parts by weight, i.e., one equivalent weight, of HCl. Hence, the equivalent weight of $NaOH = 40$.

(ii) $Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + H_2O$
$$\begin{array}{cc} 40+34 & 2 \times 36·5 \\ =74 & \end{array}$$
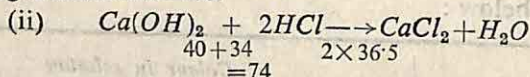
Here, 74 parts by weight of $Ca(OH)_2$ just completely neutralises 2×36·5 parts by weight, i.e., 2 equivalent weight of HCl. Hence, in order to neutralise one equivalent weight of HCl, $\frac{74}{2}$ or 37 parts by weight of $Ca(OH)_2$ will by required. Thus, the equivalent weight of $Ca(OH)_2 = 37$.

∴ Equivalent weight of a base

$$= \frac{\text{Molecular weight of the Base}}{\text{Acidity}}$$

Equivalent weight of a compound—It is that part by weight of the compound which contains one part by weight of the hydrogen-equivalent of an active element.

Example : 106 g of Na_2CO_3 contains 46 g of Na. We known that the equivalent weight of Na is 23. Thus, there are 2 Hydrogen-equivalent of the active element Na present in a molecule of Na_2CO_3.

∴ Equivalent weight of $Na_2CO_3 = \frac{106}{2} = 53$.

Normal solution—The normal solution of a substance is such a

solution one litre of which contains one gram-equivalent of the substance.

It is usually represented as (N) solution.

Thus, 1000 ml of (N) $NaOH$ contains 40 g $NaOH$.
1000 ml of (N) Na_2CO_3 contains 53 g Na_2CO_3.

Decinormal solution—The deci-normal solution of a substance is such a solution one litre of which contains 1/10th the gram-equiva-

lent of the substance. It is usually represented as $\left(\dfrac{N}{10}\right)$ solution.

Thus, 1000 ml of N/10 Na_2CO_3 contains 5·3 g Na_2CO_3.

Preparation of a Deci-normal solution of Sodium carbonate :

Method—About 10 g of pure sodium carbonate or pure sodium bicarbonate is taken in a clean and dry basin. It is carefully heated in the non-luminous flame of Bunsen burner for about 40 minutes. The basin is then cooled in a desiccator and weighed. On heating, sodium bicarbonate is completely converted into sodium carbonate.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

The process of heating, cooling and weighing is repeated till the final weight becomes constant. This indicates complete conversion of sodium bicarbonate into sodium carbonate.

Now, exactly 5·3 g of Na_3CO_3 is weighed out in a weighing bottle, and then transferred in a litre flask. A little distilled water is added to the carbonate till it goes into solution. The weighing bottle is also washed with distilled water several times and all the washings transferred into the litre flask. The solution in the flask is now diluted with distilled water and thoroughly shaken. Finally, the solution is diluted with distilled water up to the mark on the neck of the flask. The solution is now left undisturbed for about half an hour to become homogeneous. This is (N/10) solution of sodium carbonate.

Different methods of expressing the strengths of solutions :

1. The relative amounts of the solute and the solvent in a solution may be expressed as :

(a) **Per cent by weight** $= \dfrac{\text{weight of the solute}}{\text{weight of the solution}} \times 100$

(b) **Per cent by volume** $= \dfrac{\text{weight of the solute}}{\text{volume of solution in ml}} \times 100.$

2. **Normality**—Normality is defined as the number of gram equivalents of the solute present in one litre of the solution. It is represented by N.

$$\text{Normality} \quad (N) = \frac{\text{Weight of solute in g per litre of solution}}{\text{Equivalent weight}}.$$

For example : 1 (N) solution of Na_2CO_3 is obtained by dissolving 53 g of it in 1000 ml of the solution (Eq. wt. of $Na_2CO_3 = 53$).

3. Molarity—Molarity is defined as the number of moles of the solute present in one litre of the solution. It is expressed by M.

$$\text{Molarity (M)} = \frac{\text{Weight of solute in g per litre of solute}}{\text{Molecular weight}}$$

For example : 1 M solution of Na_2CO_3 is obtained by dissolving 106 g of it in 1000 ml of solution (Molecular weight of Na_2CO_3 $= 106$).

106 g of Na_2CO_3 is dissolved in sufficient amount of water in a litre flask and then more water is added to make the volume 1000 ml.

4. Molality—Molality is defined as the number of moles of the solute present in 1000 g of the solvent. It is represented by m.

$$\text{Molality (m)} = \frac{\text{Weight of solute in g per 1000 g of the solvent}}{\text{Molecular weight}}.$$

It the solvent is water then 1000 ml of water may be taken.

5. Mole fraction—Mole fraction is the ratio of the number of moles of a particular component in a solution to the total number of moles present in it. Let A and B components be present in a solution. Then, the mole fraction of A is given by

$X_A = $ Mole fraction of A

$$= \frac{\text{Number of moles of } A}{\text{Number of moles of } A + \text{Number of moles of } B}$$

$X_B = $ Mole fraction of B

$$= \frac{\text{Number of moles of } B}{\text{Number of moles of } A + \text{Number of moles of } B}$$

$\therefore \quad X_A + X_B = 1$.

Molality and Mole fractions are independent of temperature while the normality and molarity are dependent on temperature.

This method of expressing composition is frequently used for gaseous mixtures (solutions) because the partial pressures of the components of such a mixture are directly proportional to the mole fractions. For example, air is a mixture of approximately 4 moles of N_2 and 1 mole of O_2. Hence,

$$N_2 + O_2 = 5; \qquad X_{N_2} = \tfrac{4}{5} = 0 \cdot 8$$
$$X_{O_2} = \tfrac{1}{5} = 0.2$$

If the total pressure of air is P, and the partial pressure of N_2 and O_2 are p_{N_2} and p_{O_2} respectively, then

$$p_{N_2} = 0.8\ P; \qquad p_{O_2} = 0.2\ P$$

$$\therefore \quad p_{N_2} + p_{O_2} = 0.8\ P + 0.2\ P = P.$$

Inter-conversions of Strengths

1. From Percentage to Normality :

5% $NaOH$ solution means 5 g $NaOH$ present in 100 ml. Hence, 50 g $NaOH$ is present in 1000 ml. As 40 is the equivalent weight of $NaOH$, $\frac{50}{40}$ gram-equivalent $NaOH$ is present in 1000 ml.

∴   Normality of solution is $\frac{50}{40}$ (N), i.e., 1·25 (N).

10% Na_2CO_3 solution means 10 g Na_2CO_3 is present in 100 ml. Hence, 100 g Na_2CO_3 will be present in 1000 ml. As 53 is the equivalent weight of Na_2CO_3, $\frac{100}{53}$ gram-equivalent of Na_2CO_3 is present in 1000 ml.

∴   Normality of solution is $\frac{100}{53}$ (N) or 1.88 (N)

$$\text{Thus, Normality} = \frac{\text{Percentage of the substance}}{\text{Equivalent weight of the substance}} \times 10.$$

2. From Normality to Gram per litre :

Gram per litre = Normality × Equivalent weight.
2(N) HCl means (2×36.5) g of HCl per 1000 ml.

3. From Gram per litre to Normality :

$$\text{Normality} = \frac{\text{Gram per litre}}{\text{Equivalent weight}}.$$

4 g of HCl per litre means $\dfrac{4}{36.5}$ (N) $HCl = 0.109$ (N) HCl.

Important principles

(i) 1 ml (N) solution ≡ 10 ml (N/10) solution.
≡ 2 ml (N/2) solution.
≡ 50 ml (N/50) solution.
20 ml (N/10) solution ≡ $(20 \times \frac{1}{10})$ ml (N) solution.
= 2 ml (N) solution.

(ii) Acid and alkali solutions of the same normality neutralise each other in equal volumes. Thus, 10 ml (N) $NaOH$ solution will neutralise 10 ml of (N) HCl solution.

Similarly, 25 ml (N/10) Na_2CO_3 will neutralise 25 ml of (N/10) HCl solution.

(iii) In acid-base titration, we have,

$$\frac{\text{Strength of acid}}{\text{Strength of alkali}} = \frac{\text{Volume of alkali used}}{\text{Volume of acid required to neutralise it}}$$

or $\dfrac{S_1}{S_2} = \dfrac{V_2}{V_1}$;   or $V_1 \times S_1 = V_1 \times S_2$

i.e., Volume of acid $\times$ Strength of acid = Volume of alkali

$\times$ Strength of alkali.

Solved Problems

1. An aqueous solution of a dibasic acid (mole. wt. $= 118$) containing 16·6 g of the acid per litre of solution, has a density of 1·0066 g/ml. Express the concentration of solution in terms of normality, molarity, molality, mole fraction, weight per cent and volume per cent.

Solution :   Amount of solute $= 16·6$ g/litre.
Mole. wt. of solute $= 118$

$\therefore$ Moles of solute $= \dfrac{16·6}{118} = 0·14$

Volume of solution $= 1000$ ml
Density of solution $= 1·0066$ g/ml.
$\therefore$ Weight of solution $=$ Volume $\times$ Density
$= 1000 \times 1·0066 = 106·6$ g.
Weight of solvent $=$ Weight of solution $-$ weight of solute
$= 106·6 - 16·6 = 990$ g.
$\therefore$ Moles of solvent $= \dfrac{990}{18} = 55$.
$\therefore$ Total number of moles in solution $= 0·14 + 55 = 55·14$
Thus, we now get,

(i) Normality $= \dfrac{16·6}{59} = 0·281$

$\left(\text{Since the acid is dibasic hence Eq. wt.} = \dfrac{\text{Mole. wt.}}{2} = \dfrac{118}{2} = 59\right)$

(ii)   Molarity $= \dfrac{16·6}{118} = 0·14$

i.e., the solution is 0·14 M.

(iii)   Molality $= \dfrac{0·14}{990} \times 1000 = 0·1414$

i.e., the solution is 0·1414 Molal or 0·1414 m.

(iv)   Mole fraction : (a) Mole fraction of acid

$$= \frac{0 \cdot 14}{55 \cdot 14} = 0 \cdot 00254 = 2 \cdot 54 \times 10^{-3}$$

(b) Mole fraction of water $= 1 - 0 \cdot 00254 = 0 \cdot 99746 = 9 \cdot 9746 \times 10^{-1}$.

(v)   Weight per cent $= \frac{16 \cdot 6}{1006 \cdot 6} \times 100 = 1 \cdot 64\%$ by weight.

(vi)   Volume per cent $= \dfrac{\text{Weight of solute}}{\text{Vol. of solution in ml}} \times 100$

$$= \frac{16 \cdot 5}{1000} \times 100 = 1 \cdot 66\% \text{ by volume.}$$

2.   How many moles of the solute are present in the following solutions :

(a) 100 ml of 2(N) HCl; (b) 500 ml of 3(N) $NaOH$; (c) 250 ml of 20 per cent Na_2CO_3; and (d) 750 ml of 2·5 M $NaOH$.

Solution :   (a)   Normality $= \dfrac{\text{gram per litre}}{\text{equivalent weight}}$

Equivalent weight of $HCl = 36 \cdot 5$
Gram per litre = Normality × Equivalent weight.
$$= 2 \times 36 \cdot 5$$
$$= 73 \cdot 0 \text{ g litre}^{-1}.$$
∴ Amount of solute in 100 ml $= 7 \cdot 3$ g.

∴ Number of moles $= \dfrac{\text{Amount in gram}}{\text{Molecular weight}}$

$$= \frac{7 \cdot 3 \text{ g}}{36 \cdot 5 \text{ g mole}^{-1}} = 0 \cdot 2 \text{ mole.}$$

(b)   Molecular weight of $NaOH = 40$

Equivalent weight of $NaOH = \dfrac{\text{Molecular weight}}{\text{Acidity}} = \dfrac{40}{1} = 40$

Gram per litre = Normality × Equivalent weight
$$= 3 \times 40 = 120 \text{ g litre}^{-1}.$$
∴   Amount of $NaOH$ in 500 ml $= 60$ g.
∴   Number of moles $= \frac{60}{40} = 1 \cdot 5$ mole.

(c)   100 ml of 20% Na_2CO_3 solution contains 20 g of Na_2CO_3.

∴   250 ml of solution contains $\dfrac{20 \times 250}{100}$ g or 50 g of Na_2CO_3.

∴   Number of moles $= \dfrac{\text{Amount in gram}}{\text{Molecular weight}}$

Molecular weight of $Na_2CO_3 = 106$
$$\therefore \quad \text{Number of moles} = \frac{50}{106} = 0 \cdot 47 \text{ mole.}$$

(d)   2·5 M solution of $NaOH$ contains 2·5 mole of $NaOH$ per litre of solution.

$$\therefore \quad 750 \text{ ml contains} \frac{2 \cdot 5 \times 750}{1000} \text{ mole} = 1 \cdot 875 \text{ mole.}$$

3. The molarity of a solution is M_1. Calculate the volume V_2 of water to be added to V_1 ml of the solution so that its molarity may become M_2.   (I.I.T. 1977)

Solution :   Initial volume of solution $= V_1$ ml
Final volume of solution $= (V_1 + V_2)$ ml
Initial molarity of solution $= M_1$
Final molarity of solution $= M_2$

$$\therefore \quad V_1 \times M_1 = (V_1 + V_2) \times M_2; \quad \text{or} \quad V_1 M_1 = V_1 M_2 + V_2 M_2;$$
or
$$V_2 M_2 = V_1 M_1 - V_1 M_2$$

or
$$V_2 = \frac{V_1 M_1 - V_1 M_2}{M_2}.$$

4. 20 ml of a solution of (N/10) $NaOH$ required 14·6 ml of a solution of HCl for complete neutralisation. Find the strength of HCl solution (a) in terms of normality, and (b) in gram per litre.

Solution : (a) 20 ml of (N/10)$NaOH \equiv 20 \times \frac{1}{10} = 2$ ml of (N) $NaOH$
Let the strength of the acid be x (N).

$$\because \quad V_1 \times S_1 = V_2 \times S_2, \quad \therefore \quad 14 \cdot 6 \times x(\text{N}) = 2 \times (\text{N});$$

or
$$x = \frac{2}{14 \cdot 6} = 0 \cdot 136$$

$$\therefore \quad \text{Normality of } HCl \text{ solution} = 0 \cdot 136$$

(b)   Gram per litre = Normality $\times$ Equivalent weight
$$= 0 \cdot 136 \times 36 \cdot 5 = 4 \cdot 964 \text{ g litre}^{-1}.$$

5. 1000 c.c. of hydrogen chloride was dissolved in water at N.T.P. Find out the volume of sodium hydroxide solution containing 42 g of $NaOH$ per litre required to neutralise the solution of HCl.
(R. U. 1971S)

Solution : $\underset{\text{22400 c.c.}}{HCl} \quad + \quad \underset{\text{40 g}}{NaOH} \quad \rightarrow \quad NaCl \quad + \quad H_2O$

$\therefore$ 22,400 c.c. HCl (at N.T.P.) requires 40 g $NaOH$,

$\therefore$ 1000 c.c. HCl(at N.T.P.) requires $\dfrac{40 \times 1000}{22400}$ g $NaOH$

$$= 1 \cdot 78 \text{ g } NaOH.$$

Now, $\because$ 42 g $NaOH$ is present in 1000 ml solution,

$$\therefore \quad 1 \cdot 78 \text{ g } NaOH \text{ is present in } \frac{1000 \times 1 \cdot 78}{42} \text{ml solution}$$

$$= 42 \cdot 5 \text{ ml solution.}$$

6. 0·25 g of pure calcium carbonate was found to require 47 ml of dilute HCl for complete neutralisation. Calculate the normality of the acid.

Solution: $CaCO_3 + \quad 2HCl \quad \rightarrow \quad CaCl_2 + H_2O + CO_2$
$\quad\quad\quad\quad\quad\quad$ 100 $\quad\quad$ $2 \times 36 \cdot 5$
$\quad\quad\quad\quad\quad\quad\quad\quad$ or 2000 ml of
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (N) HCl
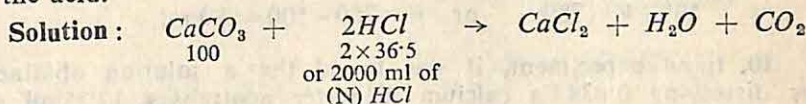
$\quad \because \quad$ 100 g of $CaCO_3$ requires 2000 ml (N) HCl,

$$\therefore \quad 0 \cdot 25 \text{ g of } CaCO_3 \text{ requires } \frac{2000 \times 0 \cdot 25}{100} \text{ml } (N) \text{ } HCl$$

$$= 5 \text{ ml (N) } HCl$$

Hence, 47 ml dil. $HCl \equiv 5$ ml (N) HCl

$\quad \therefore \quad$ Strength of HCl solution $= \frac{5}{47}$ (N) $= 0 \cdot 106$ (N).

7. 18 ml of (N/2) HCl are mixed with 20·6 ml of 2(N) HCl and 16·4 ml of (N/10) HCl. Find the strength of the mixture.

Solution :   18 ml of (N/2) $HCl \equiv \frac{18}{2}$ or 9 ml of (N) HCl.
$\quad\quad\quad\quad$ 20·6 ml of 2 (N) $HCl \equiv 20 \cdot 6 \times 2$ or 41·2 ml of (N) HCl
$\quad\quad\quad\quad$ 16·4 ml of (N/10) $HCl \equiv 16 \cdot 4 \times \frac{1}{10}$ or 1·64 ml of (N)HCl
$\quad\quad\quad\quad$ Volume of mixture $= (18 + 20 \cdot 6 + 16 \cdot 4)$ ml
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad = 55 \cdot 0$ ml.
$\quad \therefore \quad$ 55·0 ml of the mixture $\equiv (9 + 41 \cdot 2 + 1 \cdot 64)$ ml of (N) HCl
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad \equiv 51 \cdot 84$ ml (N) HCl

$$\therefore \quad 1 \text{ ml of mixture} \equiv \frac{51 \cdot 84}{55 \cdot 0} \text{ ml of (N) } HCl \equiv 0 \cdot 9425 \text{ (N) } HCl.$$

i.e.,   Strength of mixture $= 0 \cdot 9425$ (N).

8. 10·2 ml of a dilute solution of H_2SO_4 required for complete neutralisation 22·7 ml of 1·1 N/10 solution of Na_2CO_3. Find, what volume of water must be added to 400 ml of dilute H_2SO_4 solution so as to make it exactly N/10.   (Mithila U. 1973 A)

Solution :   Let the strength of dil. H_2SO_4 solution be $x(N/10)$
$\quad\quad\quad\quad \therefore \quad 10 \cdot 2 \times x(N/10) = 22 \cdot 7 \times 1 \cdot 1 \text{ (N/10)}$

or,$\quad\quad\quad\quad\quad\quad\quad x = \frac{22 \cdot 7 \times 1 \cdot 1}{10 \cdot 2} = 2 \cdot 44$

i.e.,   strength of dil. H_2SO_4 solution $= 2 \cdot 44$ (N/10).

Suppose, a ml of water added to 400ml of the dilute H_2SO_4 solution makes it N/10. Then, $(a + 400)(N/10) = 400 \times 2 \cdot 44$ (N/10)
$\quad$ or $\quad a + 400 = 400 \times 2 \cdot 44$; or $a + 400 = 976$;
$\quad$ or $\quad a = 976 - 400 = 576$ ml.

9. What volume of water must be added to 500 ml of 1·56 (N)

H_2SO_4 so as to make it exactly normal ?   (Bombay F.Y. 1974)

Solution : Initial volume = 500 ml
                    Initial strength = 1·56 (N)
Let the volume of water to be added be V ml.
∴   Final volume = $(500 + V)$ ml
        Final strength = 1(N)
∴ $500 \times 1·56 = (500 + V) \times 1$
or $500 + V = 780$;   or $V = 780 - 500 = 280$ ml.

10. In an experiment, it was found that a solution obtained by dissolving 0·0343 g calcium in water neutralises 17·25 ml of $(N/10)$ HNO_3 solution. Calculate the equivalent weight of the metal.

Solution : 17·25 ml of $(N/10)HNO_3 \equiv \dfrac{17·25}{10}$ ml of (N) HNO_3

                                        = 1·725 ml of (N) HNO_3

Now, ∵ 1·725 ml of $(N)HNO_3$ is neutralised by 0·0343 g Ca,

∴   1000   ,,   ,,   ,, $\dfrac{0·0343 \times 1000}{1·725}$ g Ca

                                        = 19·8 g Ca
∴ Equivalent weight of calcium = 19·8.

11. 1 g of the carbonate of a metal was dissolved in 25 ml of (N) HCl. The resulting solution required 50 ml of $(N/10)$ $NaOH$ for its complete neutralisation. Find the equivalent weight of the carbonate.

Solution : 50 ml of $(N/10)$ $NaOH \equiv 50$ ml of $(N/10)$ HCl
                                = 5 ml of (N) HCl
                                = acid left unused.
∴   Volume of HCl used in reaction = $(25 - 5)$ or 20 ml (N),
Now, ∵ 20 ml of (N) HCl reacts with 1 g carbonate,

∴   1000 ml   ,,   ,, $\dfrac{1 \times 1000}{20}$ g carbonate

                                        = 50 g carbonate.
i.e., Equivalent weight of carbonate = 50.

12. 1 g of a mixture of $NaOH$ and KOH was dissolved in 250 ml of water. 20 ml of this solution required 18 ml of $(N/10)$ HCl for its complete neutralisation. Calculate the percentage composition of the mixture.
                                                    (M.U. 1977A)

Solution : 20 ml solution requires 18 ml of $(N/10)$ HCl.

∴   250 ml of solution will require $\dfrac{18 \times 250}{20}$ ml $\left(\dfrac{N}{10}\right)$ HCl

        = 225 ml (N/10) HCl = 22·5 ml (N) HCl

Suppose, 1 g mixture cotains x g $NaOH$,

$\therefore$ Amount of KOH in the mixture $= (1-x)$ g.

Now, $NaOH + HCl \longrightarrow NaCl + H_2O$
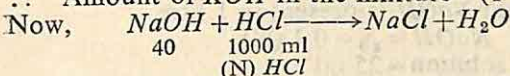
$\quad\quad\quad$ 40 $\quad$ 1000 ml
$\quad\quad\quad\quad\quad$ (N) HCl

$\because$ 40 g of $NaOH$ completely reacts with 1000 ml (N) HCl,

$\therefore$ x g $\quad$,, $\quad$,, $\quad$,, $\quad \dfrac{1000 \times x}{40}$ ml (N) HCl

$$= 25x \text{ ml (N) } HCl.$$

Now, $\quad KOH + HCl \longrightarrow KCl + H_2O$
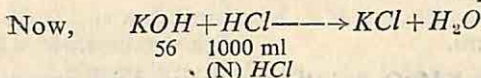
$\quad\quad\quad$ 56 $\quad$ 1000 ml
$\quad\quad\quad\quad\quad$ (N) HCl

$\because$ 56 g KOH requires 1000 ml (N) HCl,

$\therefore$ $(1-x)$ g $\quad$,, $\quad$,, $\quad \dfrac{1000(1-x)}{56}$ ml (N) HCl

$$= \dfrac{125(1-x)}{7} \text{ ml} \quad \text{,,}$$

$\therefore$ $25x + \dfrac{125(1-x)}{7} = 22 \cdot 5$

or, $\dfrac{175x + 125(1-x)}{7} = 22 \cdot 5;$ $\quad$ or $175x + 125 - 125x = 22 \cdot 5 \times 7$

or, $50x + 125 = 157 \cdot 5;$ $\quad\quad\quad\quad$ or $50x = 157 \cdot 5 - 125 = 32 \cdot 5$

$\therefore$ $\quad\quad\quad x = \dfrac{32 \cdot 5}{50} = 0 \cdot 65$

i.e., Amount of $NaOH = 0 \cdot 65$ g

$\quad\quad$ Amount of $KOH = 1 - 0 \cdot 65 = 0 \cdot 35$ g

Thus, % of $NaOH = \dfrac{0 \cdot 65 \times 100}{1} = 65\%$

$\quad\quad$ % of $KOH = \dfrac{0 \cdot 35 \times 100}{1} = 35\%.$

13. 10·0 g of a mixture of sodium chloride and sodium hydroxide containing 20% sodium hydroxide is dissolved in distilled water and the volume made up to 500 ml. Find the volume of semi-normal hydrochloric acid that will be used to neutralise 25 ml of this solution using phenolphthalein as indicator.

Solution : Weight of mixture $(NaCl + NaOH) = 10$ g

Weight of $NaOH = \dfrac{20 \times 10}{100} = 2$ g

∴   Weight of $NaOH$ present in 500 ml solution $= 2$ g
∴   Weight of $NaOH$ per litre solution $= 4$ g
i.e., $\frac{4}{40}$ gram-equivalent $NaOH$ is present in 1 litre.
Thus, the strength of $NaOH = \frac{4}{40} = 0.1$ (N)
Volume of $NaOH$ solution $= 25$ ml
Strength of $NaOH$ solution $= 0.1$ (N)
    Strength of HCl solution $= N/2$
Let the required volume of HCl solution be V ml.

∴ $25 \times 0.1 \; N = V \times \dfrac{N}{2};$ or $25 \times 0.1 = V \times \frac{1}{2}$

or $V = 2 \times 25 \times 0.1 = 5$ ml.

14. 78·5 ml of 0·108 (N) $KMnO_4$ solution is reduced in presence of acid by 5 g sample of H_2O_2. What weight of this sample of H_2O_2 will be required to oxidise 50 ml of decinormal solution of ferrous sulphate ?

Solution : 78·5 ml of 0·108 (N) $KMnO_4$
           $\equiv 78.5 \times 0.108$ ml (N) $KMnO_4$
           $= 8.478$ ml of (N) $KMnO_4$
∵ 1000 ml (N) $KMnO_4$ will reduce 17 g of H_2O_2
                                    (Eq. wt. of $H_2O_2 = 17$),

∴   8·478 ml (N) $KMnO_4$ will reduce $\dfrac{17 \times 8.478}{1000}$ g H_2O_2

                                 $= 0.144$ g H_2O_2
∴   5 g sample of H_2O_2 contains 0·144 g of pure H_2O_2.
Now, ∵ 1000 ml (N) $FeSO_4$ reacts with 17 g H_2O_2

∴   50 ml   ,,   ,, $\dfrac{17 \times 50}{1000}$ g H_2O_2

                                 $= 0.85$ g H_2O_2
∴   50 ml of (N/10) ,,   ,,   0·085 g H_2O_2.
Now, ∵ 0·144 g of pure H_2O_2 is present in 5 g sample,

∴   0·085 g   ,,   ,,   ,, $\dfrac{5 \times 0.085}{0.144}$ g $= 2.95$ g.

15. What is the molarity and molality of a 13% solution by weight of sulphuric acid ? Its density is 1·090 g/ml. To what volume should 100 ml of this acid be diluted in order to prepare a 1·5 (N) solution ?
                                                        (I.I.T. 1978)

Solution :   Calculation of molarity—
       Weight of 1 litre $H_2SO_4 = $ volume $\times$ density
                      $= 1000 \times 1.090 = 1090$ g.
       Weight of H_2SO_4 in this quantity of solution
           $= \dfrac{1090 \times 13}{100} = 141.7$ g.

$$\text{Molecular weight of } H_2SO_4 = 98$$

$$\therefore \quad \text{Moles of } H_2SO_4 = \frac{141 \cdot 7}{98}.$$

$$\therefore \quad \text{Molarity of } H_2SO_4 = \frac{141.7}{98} \Big/ 1 = 1 \cdot 445 \text{ M}.$$

Calculation of normality—

H_2SO_4 is a dibasic acid. Hence, the equivalent weight of H_2SO_4 $= \frac{1}{2} \times$ Molecular weight.

$\therefore$ Normality of $H_2SO_4 = 2 \times 1 \cdot 445 = 2 \cdot 890$ (N).

Calculation of dilution—

$$N_1 \times V_1 = N_2 \times V_2$$

$$\text{or} \quad 2 \cdot 890 \text{ (N)} \times 100 = 1 \cdot 5 \text{ (N)} \times V_2; \quad \text{or} \quad V_2 = \frac{2 \cdot 890 \times 100}{1 \cdot 5} \text{ ml}$$

$$= 186 \cdot 6 \text{ ml}$$

$\therefore$ 100 ml of the H_2SO_4 solution should be diluted to $186 \cdot 6$ ml.

Calculation of molality—

$$\text{Total weight of } H_2SO_4 \text{ solution} = 1090 \text{ g}$$
$$\text{Weight of } H_2SO_4 \text{ in it} = 141.7 \text{ g}$$
$$\therefore \quad \text{Weight of water} = 1090 - 141 \cdot 7 = 948 \cdot 3 \text{ g}$$

$$\therefore \quad \text{Molality} = \frac{141 \cdot 7}{98} \times \frac{1000}{948 \cdot 3} = 1 \cdot 54 \text{ m}.$$

16. Two litres of ammonia at 30°C and at 0·20 atmospheric pressure neutralised 134 ml of a solution of sulphuric acid. Calculate the normality of the acid. (I.I.T. 1978)

Solution : Let the volume of NH_3 at N.T.P. be x litre.

Now, $\quad P_1 = 0 \cdot 2 \qquad\qquad P_2 = 1$
$\qquad\qquad V_1 = 2 \qquad\qquad\qquad V_2 = x$
$\qquad\qquad T_1 = 273 + 30 = 303 \text{ K} \qquad T_2 = 273 \text{ K}$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}; \quad \text{or} \quad \frac{0.2 \times 2}{303} = \frac{1 \times x}{273}$$

$$\text{or} \qquad x = \frac{0 \cdot 2 \times 2 \times 273}{303} \text{ litre}$$

$$= 0 \cdot 3604 \text{ litre}.$$

$$= \frac{0 \cdot 3604}{22 \cdot 4} \text{ mole of } NH_3 = 0 \cdot 01608 \text{ mole}$$

$(\because \quad 22 \cdot 4 \text{ litre of } NH_3 \text{ at N.T.P.} = 1 \text{ mole of } NH_3).$

Ammonia is a monoacid base. Hence, its equivalent weight = its molecular weight.

0·01608 mole of NH_3 = 0·01608 gm-equivalent of NH_3

Now, 134 ml of acid solution contains 0·01608 gm-eq. of H_2SO_4

$\therefore$ 1000 ml of acid solution contains $\dfrac{0·01608 \times 1000}{134}$ gm-eq.

$= 0·12$ gm.eq. of H_2SO_4

$\therefore$ Normality of the acid = 0·12 (N)

17. A solution contains a mixture of Na_2CO_3 and $NaOH$. Using phenolphthalein as indicator, 25 ml of mixture required 19·5 ml of 0·995 (N) HCl for the end-point. With methyl orange, 25 ml of solution required 25·9 ml of the same HCl for the end-point. Calculate gm per litre of each substance in the mixture.

Solution : With phenolphthalein, $NaOH$ is completely neutralised but Na_2CO_3 is half neutralised. With methyl orange, both $NaOH$ and Na_2CO_3 are completely neutralised.

Difference of the two titre values gives the amount of HCl used to neutralise $NaHCO_3$ formed during titration with phenolphthalein as indicator. Double of this difference will give the titre value for complete neutralisation of Na_2CO_3. This difference on subtraction from the titre value with phenolphthalein gives the titre value for $NaOH$ alone.

Volume of HCl used for Na_2CO_3 in the mixture
$$= (25·9 - 19·5) \times 2 = 12·8 \text{ ml}$$

$\therefore$ $25 \times N_1 = 12·8 \times 0·995$; or $N_1 = \dfrac{12·8 \times 0·995}{25} = 0·5094$

$=$ Normality of Na_2CO_3 in the solution.

$\therefore$ Gm litre^{-1} of $Na_2CO_3 = 0·5094 \times 53 = 27$

Volume of HCl used for $NaOH$ in the mixture
$$= 19·5 - (25·9 - 19·5) = 13·1 \text{ ml}$$

$\therefore$ $25 \times N_1 = 13·1 \times 0·995$; or $N_1 = \dfrac{13·1 \times 0·995}{25} = 0·5213$

$=$ Normality of $NaOH$ in the solution.

Gm litre^{-1} of $NaOH = 0·5213 \times 40 = 20·85$

18 To a 20 ml of a copper salt solution, after necessary treatment, were added 2 gm of KI and the liberated iodine required 11·2 ml of decinormal sodium thiosulphate solution. Find out the weight of Cu^{++} ion per litre of the solution.

Solution : The equation representing the reaction between $CuSO_4$ and KI is,
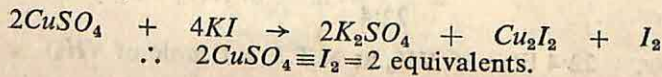
$$2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2$$
$$\therefore \quad 2CuSO_4 \equiv I_2 = 2 \text{ equivalents.}$$

$\therefore$ Equivalent weight of $CuSO_4$ = Molecular weight of $CuSO_4$.

$\therefore$ Equivalent weight of Cu^{++} ion = At. wt. = 63·5

Volume of thiosulphate solution = 11·2 ml.

Strength of thiosulphate solution = 0·1 N

$\therefore$ 11·2 ml 0·1 N thiosulphate solution = 1·12 ml N soln.

20 ml of Cu salt solution of unknown strength reacts with 1·12 ml of N thiosulphate solution.

$$\therefore \quad 20 \times S = 1·12 \text{ N}; \quad \therefore \quad S = \frac{1·12}{20} \text{N}$$

$$\therefore \quad \text{Weight of } Cu^{++} \text{ ion present/litre} = \frac{1·12 \times 63·5}{20} = 3·556 \text{ gm.}$$

Questions

Long Answer Type :

1. What do you mean by equivalent weight of an acid ? How would you prepare an exactly (N/10) solution of Na_2CO_3 in the laboratory ?

2. What do you mean by the following ?—

(a) Acidimetry and Alkalimetry, (b) standard solution, (M. U. 1973 S; P. U. 1976 A), (c) Normal solution, (d) Factor (P. U. 1976 A), (e) Indicator (M. U. 1973 S) and (f) Normality of a solution.

3. Describe the different methods for expressing the strengths of solutions.
(B. U. 1970 A)

Short Answer Type :

1. Define 'Normality.'

2. Find the equivalent weight of oxalic acid. [Ans. Oxalic acid ($H_2C_2O_4$) is a dibasic acid. Hence, equivalent weight = $\dfrac{\text{Molecular weight}}{\text{Basicity}} = \dfrac{90}{2} = 45$]

3. Distinguish between **molarity** and **molality**.

4. Show that the sum of the mole fractions of the solute and the solvent is unity.

5. How is it that although they are of the same strength yet 10ml of 5% $NaOH$ solution do not exactly neutralise 10 ml of 5% HCl solution ?

Numerical Problems :

1. 20ml of a solution of Na_2CO_3 in water required 8.2ml of (N/10) HCl for complete neutralisation. Find the strength of Na_2CO_3 solution—(a) in terms of normality and (b) in gram per litre. [Ans. (a) 0·041 (N); (b) 2·173 g]

2. How many ml of a solution of decinormal potassium hydroxide will be required to neutralise 19·8 ml of a semi-normal HCl ? (Ans. 99 ml)

3. 25 ml of HCl liberate 10 ml of CO_2 at N.T.P. when treated with excess of pure $CaCO_3$. Calculate the normality of HCl solution. (Ans. 0·0357 (N)]

4. What volume of a 5% solution of Na_2CO_3 will be required to nautralise a litre of (N/10) H_2SO_4 ? (Ans. 106 ml)

5. A piece of magnesium ribbon is completely dissolved in 40 ml of (N/10) HCl. The excess of acid required 16 ml of (N/5) $NaOH$ solution for complete neutralisation. Find the weight of magnesium. (Ans. 0·012g)

6. 2g of a mixture of $NaCl$ and NH_4Cl is heated with 50 ml of (N) $NaOH$ till NH_3 is driven off. The excess of alkali required 20ml of (N) H_2SO_4 for neutralis-ation. What is the percentage of NH_4Cl in the mixture ?   (Ans. 80·25%)

7. 10ml of (N/10) Na_2CO_3 solution neutralised 7ml of dilute H_2SO_4. How much water must be added to 100ml of the acid to make it (N/10) ?   (Ans. 42·857 ml)

8. 11·32 ml of 0·901 (N/2) $NaOH$ neutralise 10 ml of H_2SO_4 containing 0·02499 g per ml. Find the molecular weight of $NaOH$.   (Ans. 40)

9. What volume of N/2 HCl must be diluted to give 2 litre of N/5 HCl ? (Kurukshetra Univ. 1977)   (Ans. 800ml)

10. 100 ml of 0·1 (N) sulphuric acid solution is mixed with 150 ml of 0·2(N.) sulphuric acid solution. What is the normaiity of the resulting mixture ?   [Ans] [Ans. 0·16 (N)]

11. What amount of sodium hydroxide is present in 250 ml of its decinormal solution ? ($Na=23·0$)   Ans. 1g litre^{-1})

12. 20·0 ml of a solution of sulphuric acid neutralises 24·5 ml of a solution of sodium carbonate containing 2·65g per 100ml. How much water should be added to 100ml of the sulphuric acid solution to make its strength decinormal ?   (Ans. 512·5 ml)

13. A solution of sulphuric acid (mole. wt.$=98$) containing 980 g of the acid per litre of solution has a density of 1·84 g/ml. Express the concentration of solution in terms of normaiity, molarity, molality, mole fraction, weight percent and volume percent. (Ans. Normality$=20$ N; molarity$=10$ M; molality$=11·3$ ml
Mole fraction acid$=0·173$, mole fraction water$=0·827$;
wt. per cent$=53·2\%$; Vol. per cent$=98\%$).

14. An aqueous solution of $NaCl$ contains 8·00 g of the salt per 100 g of solution at 25°C. Calculat the concentration of this solution on molal scale.   (Ans. 1·486 m)

Objective Questions :

1. The suitable indicator for the titration of a strong acid and a weak base is
   (i) litmus (ii) phenolphthalein (iii) methylorange (iv) phenol-red.

2. The pH of solution obtained by complete neutra lisation of acetic acid by sodium hydrozide solution will be
   (i) exactly 7, (ii) more than 7, (iii) less than 7, (iv) zero.

3. In the titration of oxalic acid with caustic soda solution the indicator used is
   (i) methylorange, (ii) methyl red, (iii) fluorescein. (iv) phenolphthalein.

4. 100 ml of 0·2 M CH_3COOH are mixed with 50 ml of 0·2 M $NaOH$. The nature of the remaining solution is
   (i) highly acidic, (ii) highly basic, (iii) neutral, (iv) simply acidic.
                                                              (PMDT 1977)

5. 10ml of N $NaOH$ is diluted to 100ml. The strength of the diluted solution is
   (i) 10 N, (ii) 100 N, (iii) 0·01 N, (iv) 0·1N

6. The volume of N/10 $NaOH$ solution required to neutralise 10 ml of 0·1 N HCl is
   (i) 10 ml, (ii) 1 ml (iii) 100 ml (iv) 20m l.

7. 10 ml N HCl is mixed with 20 ml N $NaOH$. The mixture will be neutralised by adding
   (i) 10 ml N $NaOH$ (ii) 20 ml $NHCl$ (iii) 10ml N HCl.

8. 10 g of a base is neutralised by 250 ml N HCl. The equivalent weight of the base is
   (i) 10, (ii) 40, (iii) 20. (iv) 30.

9. 500 ml N $NaOH$ contains

(i) 40 g $NaOH$, (ii) 1 gm eq. $NaOH$, (iii) 20 g $NaOH$.

10. 100 ml N-H_2SO_4 reacts with 1·2 g of a metal. The equivalent weight of the metal is

(i) 0·12, (ii) 24, (iii) 10, (iv) 12.

11. What is the normality of 7·3% (wt/wt.) HCl solution (mole. wt. of HCl= 36·5) ?

(i) 0·5, (ii) 3·0 (iii) 4.0 (iv) 2·0.   (MDAT 1977)

12. The molarity of a solution of sodium chloride (mole. wt.=58·5) in water containing 5·85 g of $NaCl$ in 500 ml solution is

(i) 0·25, (ii) 2·3, (iii) 1·0, (iv) 0·2 (v) 0·5.   (MDAT 1980)

13. When 14 g of phosphoric acid (Mol. wt.=98) is dissolved in 250 g of water, the resulting solution will be

(i) 0̄·11 Molar, (ii) 0·57 Molar, (iii) 0·19 Normal, (iv) 0·28 Normal.

14. For correct results in all acid-base titrations the indicator must change colour at a pH :

(i) slightly greater than 7, (ii) slightly less than 7, (iii) equal to 7, (iv) equal to that at the stoichiometric point.

15. What will be the volume of a 5% solution of H_2SO_4 required for the neutralization of 500 ml of $N/3$ $NaOH$?

(i) 245 ml, (ii) 24·5 ml, (iii) 2·45 ml, (iv) None.

16. What volume of water must be added to a litre of 1·123 N acid solution to make it exactly normal acid solution ?

(i) 12·3 ml, (ii) 123 ml, (iii) 1·23 ml, (iv) None of these.

17. How many grams of Na_2CO_3 is required to prepare 500 ml of N/10 solution?

(a) 5·3 g, (b) 10·6 g, (c) 2·65 g, (d) 13·25 g.

18. Oxalic acid is a dibasic acid, having molecular formula, $H_2C_2O_4$. $2H_2O$.

(a) What weight of oxalic acid is required to prepare 500ml of 0·1 molar solution ?

(i) 12·6 g, (ii) 6·3 g, (iii) 4·5 g, (iv) 9 g.

(b) What weight of oxalic acid is required to prepare 1000 ml of N/10 solution ?

(i) 9 g, (ii) 12·6 g, (iii) 6·3 g, (iv) 4·5 g.

19. What will be the volume of a 4% solution of $NaOH$ required for complete neutralisation of a 250 c.c. N/8 HCl ?

(i) 3·125ml, (ii) 0·3125ml, (iii) 31.25ml, (iv) 312·5 ml.

20. What will be the normality of phosphoric acid solution (sp. gravity 1·426 and containing 98% by weight of pure H_3PO_4) ?

(i) 42·78 N, (ii) 4·278 N, (iii) 14·26 N, (iv) 427·8 N.

21. What will be the volume of a 8% solution of $AgNO_3$ necessary for the neutralisation of 30 c.c. N/20 $Na_2S_2O_3$?

(i) 31·87 ml (ii) 3·187 ml (iii) 0·3187 ml (iv) none of these.

22. What will be the molarity of the phosphoric acid solution (sp. gravity= 1.426 and containing 98% by weight or pure H_3PO_4) ?

(i) 1·426 M, (ii) 14·26 M, (iii) 142·6 M, (n) none of these.

□ □ □

ACID, BASES AND SALTS

Concepts of Acids and Bases :

The terms **acid** and **base** apply to two different groups of chemical substances with widely opposing sets of characteristics. Some of the hitherto accepted concepts to explain the behaviour of acids and bases are discussed here.

1. Arrhenius concept (1884)—In the light of this concept, an **acid is defined as a substance that releases protons in aqueous solution,** and **a base is defined as a substance that releases hydroxides ions in aqueous solution.**

Acids :
$$HCl \rightarrow H^+ + Cl^-$$
$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$
Bases :
$$NaOH \rightarrow Na^+ + OH^-$$
$$Ca(OH)_2 \rightarrow Ca^{++} + 2OH^-$$
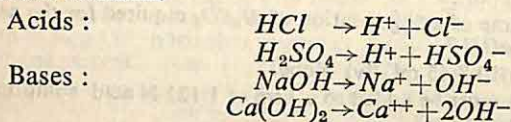
A neutralisation reaction between an acid and a base gives salt and water.

$$HA + BOH \rightarrow BA + H_2O$$
$$\text{(acid)} \quad \text{(base)} \quad \text{(salt)} \quad \text{(water)}$$
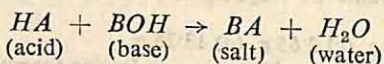
Many neutralisation reactions in aqueous solution can be properly explained by Arrhenius equation. But this concept is, however, tied to the solvent water. Besides, the substances containing hydroxide ions, there are many which show basic properties in aqueous solution.

2. Solvent-System concept—In this concept, **the solvent is capable of producing cations that correspond to the acid and anions that correspond to the base.** For example, water is capable of producing H_3O^+ and OH^-. These two ions correspond to the Arrhenius acid and Arrhenius base.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$\text{(Arrhenius} \qquad \text{(Arrhenius}$$
$$\text{acid)} \qquad \text{base)}$$
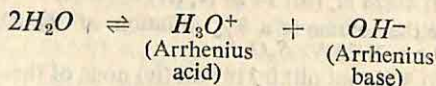
Ammonia undergoes autoionization in a way similar to water.

$$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
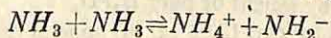
Other solvents such as acetic acid and sulphuric acid are also capable of under going autoionization.

3. Brönsted-Lowry Concept (1923)—According to this concept, an **acid** is a substance that releases protons and a **base** is a substance that combines with protons. In other words, an acid is a proton-

donor, whereas a base is a proton-acceptor.

$$\text{Acid}_1 \rightleftharpoons H^+ + \text{Base}_1 \qquad \qquad \text{..} \quad \text{(i)}$$

$$\text{Base}_2 + H^+ \rightleftharpoons \text{Acid}_2 \qquad \qquad \text{..} \quad \text{(ii)}$$

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1 \qquad \text{..} \quad \text{(iii)}$$
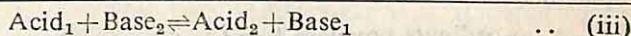
The acid and base represented in equation (i) and (ii) constitute a conjugate pair. That is, an acid forms its conjugate base by the loss of a proton. Similarly, a base forms its conjugate acid when it gains a proton. Thus, Acid_1 and Base_1 are conjugate pair, and similarly, Base_2 and Acid_2 are conjugate pair.

Acid_1	$+$	Base_2		Acid_2	$+$	Base_1
H_3O^+	$+$	OH^-	$\rightleftharpoons$	H_2O	$+$	H_2O
HCl	$+$	H_2O	$\rightleftharpoons$	H_3O^+	$+$	Cl^-
H_2O	$+$	NH_3	$\rightleftharpoons$	NH_4^+	$+$	OH^-
H_2O	$+$	CO_3^{--}	$\rightleftharpoons$	HCO_3^-	$+$	OH^-
H_2O	$+$	HCO_3^-	$\rightleftharpoons$	H_2CO_3	$+$	OH^-
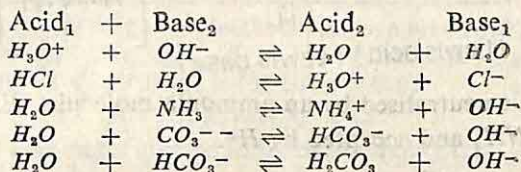
The conjugate base of a strong acid is weak. Thus, Cl^- ion, the conjugate base of the strong acid HCl, is a poor proton-acceptor.

The conjugate base of a weak acid is strong. Thus, the weak acid H_2O has a strong conjugate base OH^-.

Water behaves as a proton-donor as well as a proton-acceptor depending upon what else is present. With HCl, it acts as a proton-acceptor or a base, but with NH_3, it acts as a proton-donor or an acid.

$$HCl \ + \ H_2O \ \rightleftharpoons \ H_3O^+ + \ Cl^-$$
(Acid) (Base)

$$NH_3 \ + \ H_2O \ \rightleftharpoons \ NH_4^+ + \ OH^-$$
(Base) (Acid)
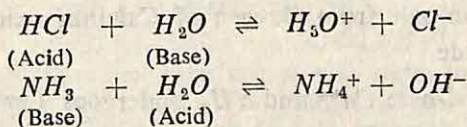
The relative strength of an acid is a measure of its ability to donate a proton. Similarly, the relative strength of a base is a measure of its ability to accept a proton. Any two substances that compete to donate protons, the one that donates protons over the other is more acidic. Thus, H_2O in reaction with NH_3 is an acid, whereas H_2O in reaction with HCl is a base.

4. Lewis Concept (1923) : Lewis defined an acid and a base as follows :

An acid is a molecule or ion that can accept an electron-pair from another molecule or ion.

A **base** is a molecule or ion that can donate an electron-pair to an acid.

Thus, an acid is an electron-pair acceptor and a base is an electron-pair donor.

A co-ordinate covalent bond is formed when a Lewis acid reacts with a Lewis base. This is actually the neutralisation reaction.

Examples :

(i)

$$H^+ + \overset{\displaystyle H}{\underset{\displaystyle H}{:N:H}} \longrightarrow \left[\overset{\displaystyle H}{\underset{\displaystyle H}{H:N:H}}\right]^+$$

(Lewis acid) (Lewis base)
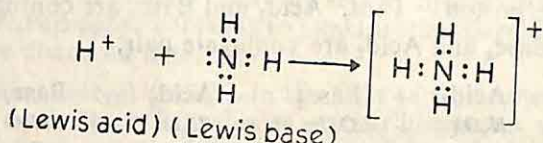
H^+ ion is neutralised by an ammonia molecule. Electron-pair is donated by NH_3 and accepted by H^+.

(ii)

$$\overset{\displaystyle H}{\underset{\displaystyle H}{H:N:}} + \overset{\displaystyle :F:}{\underset{\displaystyle :F:}{:B:F:}} \longrightarrow \overset{\displaystyle H}{\underset{\displaystyle H}{H:N:}} \ \overset{\displaystyle :F:}{\underset{\displaystyle :F:}{:B:F:}}$$

(Lewis base) (Lewis acid)　　Boron trifluoride ammonia

$$[Ca]^{++} \ [:\ddot{O}:]^{--} + \overset{\displaystyle :\ddot{O}:}{\underset{\displaystyle :\ddot{O}:}{:\ddot{S}:O:}} \longrightarrow [Ca]^{++} \left[:\ddot{O}: \overset{\displaystyle :\ddot{O}:}{\underset{\displaystyle :\ddot{O}:}{\ddot{S}}} :\ddot{O}:\right]^{--}$$
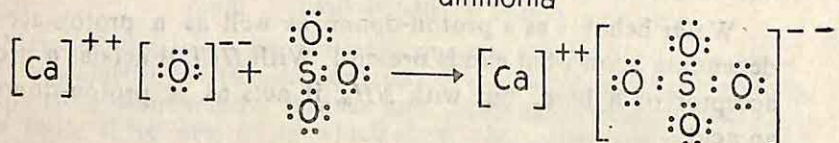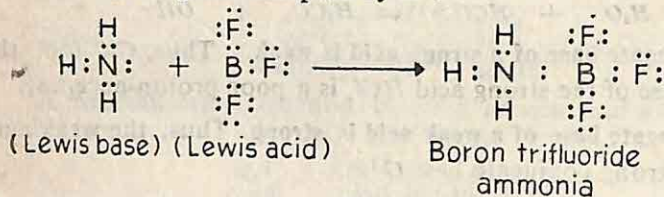
An electron-pair from Oxygen of Calcium oxide is donated to Sulphur trioxide.

(iv) An acid-base Cu^{++} and NH_3 undergoes Lewis neutralisation by forming four co-ordinate bonds.

(iii)

$$Cu^{++} + 4:NH_3 \longrightarrow \left[\begin{matrix} H_3N: & & :NH_3 \\ & Cu & \\ H_3N: & & :NH_3 \end{matrix}\right]^{++}$$

(Lewis acid)　　(Lewis base)
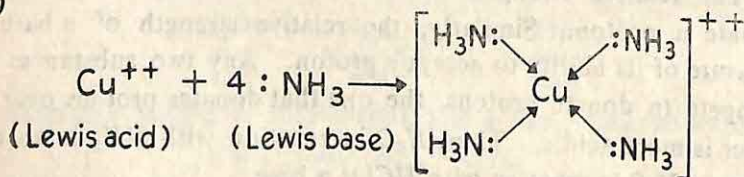
Explanation : A Lewis acid lacks an electron-pair in an empty orbital, or it has an orbital that can be made available and a Lewis base has a non-bonding electron pair and it can supply this pair to another substance lacking in electron-pair.

Lewis Acids and Lewis Bases

Acid		Base		Product
HCl	+	NH_3	$\rightarrow$	$NH_4^+ + Cl$
Al^{3+}	+	$6H_2O$	$\rightarrow$	$[Al(H_2O)_6]^{3+}$
BF_3	+	F^-	$\rightarrow$	BF_4^-
$AuCl_3$	+	Cl^-	$\dashrightarrow$	$AuCl_4^-$
SiF_4	+	$2\ddot{\underset{..}{F}}:^-$	$\dashrightarrow$	SiF_6^{2-}

Lewis acids that accept an electron-pair are **electrophilic.**
H_2O is a stronger base than Cl^-. This is because H_2O displaces Cl^- in supplying an electron-pair for the proton.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
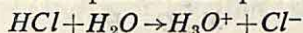
∴ H_2O is a stronger nucleophilic agent than Cl^-.

Oxides

An oxide is a binary compound of Oxygen and another element. There are two classes of oxides—**acidic** and **basic.**
An **acidic oxide** is one that dissolves in water to produce an acid.

$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$SO_3 + H_2O \rightarrow H_2SO_4$$
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$
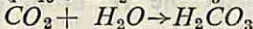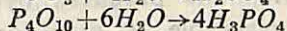
The oxides SiO_2, B_2O_3 etc. are insoluble in water.
But they neutralise bases and are, therefore, acidic.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$B_2O_3 + 2NaBOH \rightarrow 2NaBO_2 + H_2O$$
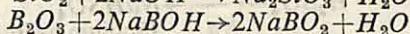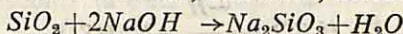
Basic oxides are those that react either with water to form bases or with acids to produce salts. Thus, K_2O, CaO and Al_2O_3 are the parent oxides of KOH, $Ca(OH)_2$ and $Al(OH)_3$ respectively.

Amphoterism

There are some substances which behave both as an acid and a base. These substances are called **amphoteric**, and such a property is referred to as **amphoterism.** $Al(OH)_3$ is one of such substances.

$$Al(OH)_3$$
(as an acid)   (as a base)

$$H_3AlO_3 \qquad\qquad Al(OH)_3$$

$$3H^+ + AlO_3^{---} \qquad\qquad Al^{+++} + 3OH^-$$
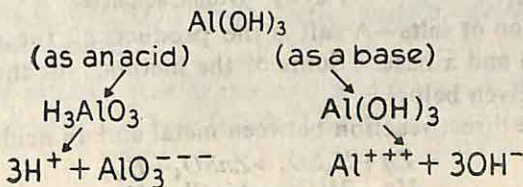
The amphoteric character of $Al(OH)_3$ depends on whether a stronger base or a stronger acid is used. If a stronger base (i.e., $NaOH$) is used, aluminium acts as an acid and it appears in the anion.

$$Al(OH)_3 + NaOH \rightarrow NaAlO_3 + 2H_2O$$
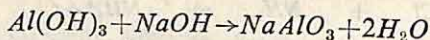
In case, a stronger acid (i.e., HCl) is used, aluminium acts as a base and it appears in the cation.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$
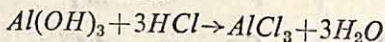
The amphoteric property is shown by hydroxides of metals like Zn, Cr, Pb and Sn, in addition to Al. The cause of amphoterism of an oxide or hydroxide is the central atom X in the system $X—O—H$. The central atom X possesses an ionisation potential which allows both $X—O$ and $O—H$ bonds to break with equal facility.

$$X \vdots O \vdots H$$
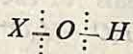
If $X—O$ bond breaks, the substance acts as a base, but when $O—H$ bond breaks the substance acts as an acid.

The ions whose ionisation potentials lie within the range 3·5 to 9·5 tend to be amphoteric.

Salts

Def.—A salt is a compound produced by the partial or total replacement of the replaceable H atom or atoms present in the molecule of an acid by a metal or a group of elements acting as a metal.

$$H_2SO_4 \xrightarrow[+Na]{-H} NaHSO_4 \quad \text{(Sodium hydrogen sulphate)}$$

$$H_2SO_4 \xrightarrow[+2Na]{-2H} Na_2SO_4 \quad \text{(Sodium sulphate)}$$

$$H_2SO_4 \xrightarrow[+(NH_4)]{-H} NH_4HSO_4 \quad \text{(Ammonium bisulphate)}$$

$$H_2SO_4 \xrightarrow[+2NH_4]{-2H} (NH_4)_4SO_4 \quad \text{(Amm. sulphate)}$$
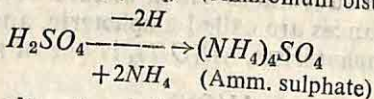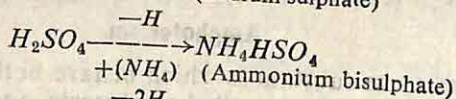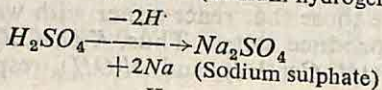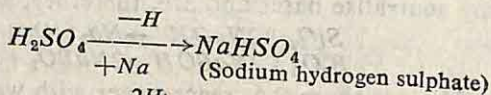
Preparation of salts—A salt is the product of the reaction between an acid and a base. Some of the methods for the preparation of salts are given below :

(i) By the direct reaction between metal and an acid.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$
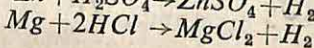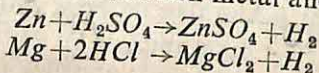
(ii) By the reaction between a base and an acid (nentralisation reaction).

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
$$NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$$
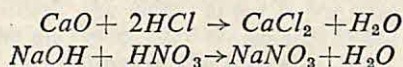
(iii) By the direct union between a metal and a non-metal.

$$2Na + Cl_2 \rightarrow 2NaCl$$
$$Fe + S \rightarrow FeS$$
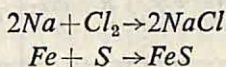
(iv) By the union between an acidic oxide, and a basic oxide.

$$CO_2 + CaO \rightarrow CaCO_3$$
$$SO_3 + Na_2O \rightarrow Na_2SO_4$$
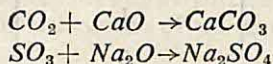
(v) By reaction between a metal and a base, for example, when zinc is boiled with caustic soda solution, sodium zincate is produced.

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$$
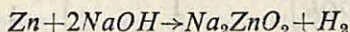
Classification of salts—Salts are of following types

(i) **Normal salt**—A salt which is formed by the total replacement of the replaceable H-atoms present in the molecule of an acid by a metal (or a group) is known as the **normal salt**. Thus, Na_2SO_4, $(NH_4)_2SO_4$ etc. are normal salts.

(ii) **Acid salt**—A salt formed by the partial replacement of the replaceable H-atoms present in the molecule of an acid by a metal (or group) is known as an Acid salt. Thus, $NaHSO_4$, NH_4HSO_4 etc. are acid salts.

Barium acid arsenate ($BaHAsO_4$), Sodium dihydrogen phosphate (NaH_2PO_4), Cupric biarsenite ($CuHAsO_3$) and Potassium bitartrate ($KHC_4H_4O_6$) are also acid salts.

(iii) **Basic salt**—A basic salt is formed when an acid reacts with a larger amount of a base than is necessary for the formation of a normal salt. Thus, $CaCO_3$, $2PbCO_3.Pb(OH)_2$ etc. are basic salts. Basic aluminium acetate, $Al(OH)(C_2H_3O_2)_2$; Basic copper carbonate, $CuCO_3.Cu(OH)_2$; Basic ferric acetate, $Fe(OH)(C_2H_3O_2)_2$ etc. are also basic salts.

(iv) **Mixed salts**—Mixed salts are formed from partial neutralisation of an acid with one base followed by further neutralisation by another base.

Example : $Na(NH_4)HPO_4$, $LiKCO_3$, $KMgPO_4$ etc.

Basicity of an acid—The basicity of an acid is measured by the number of replaceable Hydrogen atom or atoms present in a molecule of the acid.

Example :

Acid	Number of Replaceable Hydrogen atom	Basicity
HCl	1	1
HNO_3	1	1
H_2SO_4	2	2
H_3PO_4	3	3
$HCOOH$	1	1
CH_3COOH	1	1

An acid containing **one** replaceable H atoms in a molecule is called a **monobasic acid**. For example, HCl, HNO_3, $HCOOH$ (formic acid), CH_3COOH (acetic acid) etc. are **monobasic acids**.

Acids containing **two** replaceble H atoms in a molecule are known as **dibasic acids**. For example, H_2SO_4, $H_2C_2O_4$ (oxalic acid) etc. are **dibasic acids**.

Similarly, H_3PO_4 (Phosphoric acid) is a **tribasic acid**.

Acidity of a base—The acidity of a base is measured by the number of hydroxyl groups present in a molecule of the base.

Monoacidic bases : $NaOH$, KOH etc.
Diacidic bases : $Cu(OH)_2$, $Ca(OH)_2$, $Zn(OH)_2$ etc.
Triacidic bases : $Bi(OH)_3$, $Al(OH)_3$.

For bases containing no hydroxyl group, the acidity is determined by the number of molecules of the base required to just react with one molecule of a monobasic acid.

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
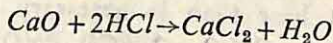
Here, 1 molecule of CaO reacts with 2 molecules of HCl. This means, 1 molecule of CaO is equivalent to 2 molecules of HCl. As HCl is monobasic, CaO most be diacidic. Acidity of CaO is, therefore, **two**.

Ionic Equilibria

Water is the most common reaction medium in chemistry. Many water-soluble substances form aqueous solutions that contain ions. The formation of ions in solution is attributed to two sources :

(i) Ions already exist in the pure solute. For example, Sodium chloride ($NaCl$) solid is made up of Na^+ and Cl^- ions. When it is dissolved in water, the Na^+ and Cl^- ions become separated from each other. The energy needed to do this is supplied by the energy of hydration of these ions by the water.

$$Na^+Cl^-(s) + H_2O \rightleftharpoons Na^+(aq) + Cl^-(aq)$$
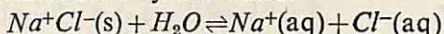
(ii) The solvent chemically reacts with the solute. The chemical bonding of the soulute is, thus, broken. For example, hydrogen chloride ($H—Cl$) is a gas under ordinary conditions. It is composed of covalent molecules. When HCl gas is dissolved in water, the HCl gives up its proton to water forming hydroxonium ion, H_3O^+. Hence, a solution of HCl in water is made of the hydrated ions, H_3O^+ and Cl^- ions.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$
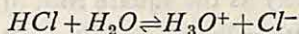
Both of the above processes are **equilibrium processes.** There exists a condition of equilibrium between the ions in solution and the unionised molecules.

Complete ionisation—Strong electrolytes are completely ionised in aqueous solution. For example, HCl and $NaOH$ become completely dissociated into ions when dissolved in water.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$NaOH(s) + H_2O \rightarrow Na^+(aq) + OH^-(aq)$$
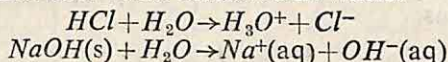
These two reactions go to completion. Hence, we do not use an equilibrium constant for them.

Partial ionisation—Weak electrolytes are only partially dissociated into ions. Acetic acid is a weak acid. It dissociates into ions to the extent of about 1% in aqueous solutions. The equilibrium constant concept may be applied to it.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
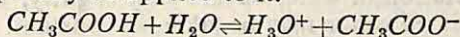
$$K = \frac{[H_3O^+] \times [CH_3COO^-]}{[CH_3COOH] \times [H_2O]}$$

The concept of equilibrium may also be applied to slightly soluble salts like $AgCl$, $PbCrO_4$, CdS etc., even though they are completely ionised in aqueous solutions.

Ostwald's Dilution Law

The dissociation of acetic acid may be represented as

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
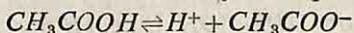
	CH_3COOH	H^+	CH_3COO^-
Initially :	c	0	0
At equil. :	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Let c moles of acitic acid be dissolved per litre of an aqueous solution. Let α be its degree of dissociation. Then, at equilibrium, concentration of undissociated acetic acid $= c(1-\alpha)$

concentration of H^+ ions $= c\alpha$

concentration of CH_3COO^- ions $= c\alpha$

$\therefore$ Equilibrium constant, $K = \dfrac{ca\,ca}{c(1-\alpha)} = \dfrac{c\,\alpha^2}{(1-\alpha)}$.

This is the mathematical expression of **Ostwald's dilution law**. K is called the **dissociation constant** of the acid. It is constant at a given temperature.

If α is very small then

$$K = c\alpha^2$$

i.e., $\alpha = \sqrt{\dfrac{K}{c}}$;   or $\alpha \propto \dfrac{1}{\sqrt{c}}$

i.e., the degree of dissociation of a very weak acid or any weak electrolyte varies inversely as the square root of concentration.

The Ostwald's dilution law is found to hold good for weak electrolytes. The law, however, fails when applied to strong electrolytes.

Ionic Product of Water :

Water is a very weak electrolyte. It dissociates very slightly into H^+ and OH^- ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$
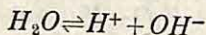
Applying the Law of Mass Action, we have

$$K = \dfrac{[H^+] \times [OH]^-}{[H_2O]}; \qquad \text{or} \qquad [H^+] \times [OH^-] = K[H_2O]$$

As the dissociation of water occurs only slightly, the concentration of undissociated water may be taken as constant. Hence,

$$[H^+] \times [OH^-] = K_W.$$

The constant K_W is known as **ionic product of water**. The value of K_W at 25°C is 1×10^{-14}.

Neutral, Acid and Basic solutions :

In pure water, $[H^+] = [OH^-] = 1 \times 10^{-7}$ mole/litre.

In acidic solution, $[H^+] > [OH^-]$, i.e., $[H^+]$ is greater than 10^{-7} mole litre^{-1}.

In alkaline solution, $[H^+] < [OH^-]$, i.e. $[H^+]$ is less than 10^{-7} mole litre^{-1}.

However, the value of K_W is the same, whether the solution is acidic, alkaline or neutral.

The pH scale : The acidity or alkalinity of a solution is expressed by *pH*. The *pH* of a solution is defined as logarithm of the reciprocal of hydrogen ion concentration, expressed in mole litre^{-1}.

Thus,

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]; \quad \text{or} \quad [H^+] = 10^{-p^H}$$

For pure water, $[H^+] = 10^{-7}$.

$\therefore \quad pH = -\log 10^{-7} = -(-7)\log 10 = 7$.

For pure water or neutral solution $pH = 7$.

For acidic solution $pH < 7$.

For alkaline solution $pH > 7$.

The smaller the pH of a solution, the greater the acidity.

Similarly, $\quad pOH = \log \frac{1}{[OH^-]} = -\log[OH^-]$

$$pH + pOH = 14·00 \text{ (at } 25°C).$$

I fthe pH of a solution is 4, its $pOH = 14 - 4 = 10$.

The smaller the pOH, the greater the alkalinity.

The following table will make the above relation clear.

$[H^+]$ mole litre	OH^- mole litre^{-1}	pH	pOH	
10^0	10^{-14}	0	14	Strongly acidic
10^{-1}	10^{-13}	1	13	
10^{-3}	10^{-11}	3	11	
10^{-5}	10^{-9}	5	9	Weakly acidic
10^{-7}	10^{-7}	7	7	Neutral
11^{-9}	10^{-5}	9	5	Weakly basic
10^{-14}	10^0	14	0	Strongly basic

pK Notation : The pK_A is defined as

$$pK_A = \log \frac{1}{K_A} = -\log K_A.$$

pK_A is often used to express the strength of an acid or base. Thus, an acid whose ionisation constant is 10^{-4} has a $pK_A = 4$.

Similarly, $pK_B = -\log K_B$.

Numericals

1. The ionisation constant of formic acid is $1·8 \times 10^{-4}$. What is the percentage ionisation of a $0·0010$ M solution of this acid ?

Solution : $\quad HCOOH \rightleftharpoons H^+ + HCOO^-$
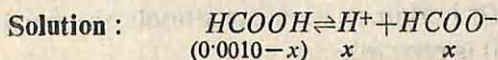
$\quad\quad (0·0010-x) \quad\quad x \quad\quad x$

Let equilibrium concentrations of H^+ and $HCOO^-$ ions be x each.

$\therefore$ $[HCOOH] = (0.0010 - x)$

$\therefore$

$$K_A = \frac{[H^+] \times [HCOO^-]}{[HCOOH]} = \frac{x \times x}{(0.0010 - x)}$$

$$= \frac{x^2}{0.0010} \quad \text{(assuming } x \text{ to be very small)}.$$

$\therefore$

$$1.8 \times 10^{-4} = \frac{x^2}{0.0010}; \quad \text{or} \quad x^2 = 0.0010 \times 1.8 \times 10^{-4}$$

or

$$x = 4.2 \times 10^{-4}.$$

$\therefore$ Percentage ionisation $= \dfrac{4.2 \times 10^{-4}}{0.0010} \times 100$

$$= \frac{4.2 \times 10^{-4}}{10^{-3}} \times 10^2 = 42\%.$$

2. Calculate the pH value of $4.9 \times 10^{-4} N$ acid, assuming complete ionisation.

Solution : $[H^+] = 4.9 \times 10^{-4}$ mole litre^{-1}

$\therefore$ $pH = \log \dfrac{1}{4.9 \times 10^{-4}} = \log 10^4 - \log 4.9$

$$= 4 - 0.69 = 3.31.$$

3. The pH value of a solution is 4, calculate the hydrogen ion concentration of the solution.

Solution : $[H^+] = 10^{-pH} = 10^{-4}$ mole litre^{-1}.

Common Ion Effect :

When a solution of a **weak acid** or a **weak base** is treated with some ions common to the acid or base, the degree of ionisation of the acid or base is suppressed. For example, if some acetate ion (as sodium acetate) is added to a solution of acetic acid, the ionisation of acetic acid is considerably reduced.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^- \qquad \text{.. (i)}$$
$$CH_3COONa \rightarrow CH_3COO^- + Na^+ \qquad \text{.. (ii)}$$
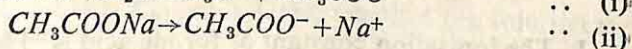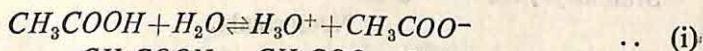
CH_3COO^- ions from the ionisation of CH_3COONa increase the concentration of CH_3COO^- ions in solution. As a result, the reaction represented by equation (i) is reversed.

Similarly, if to a solution of NH_4OH some NH_4^+ ions are added in the form of NH_4Cl, the ionisation of NH_4OH is suppressed to a large extent.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$
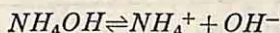
The effect on the ionisation of the acid or base on the addition of the common ion is known as the Common Ion Effect.

Strength of Acids and Bases

An acid is a proton-donor whereas a base is a proton-acceptor. A substance may act as an acid under one set of conditions and as a base in another. The competition for protons between two sub-stances determines their relative strengths as acids or bases.

The following factors determine the relative strengths of acids and bases :

1. Ionisation Constant—An acid HA dissociates as
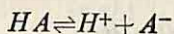
$$HA \rightleftharpoons H^+ + A^-$$

$$\therefore \quad K_A = \frac{[H^+] \times [A^-]}{[HA]} \qquad \qquad .. \quad \text{(i)}$$

where, K_A is the dissociation constant of the acid HA.

A base dissociates as
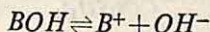
$$BOH \rightleftharpoons B^+ + OH^-$$

$$\therefore \quad K_B = \frac{[B^+] \times [OH^-]}{[BOH]} \qquad \qquad .. \quad \text{(ii)}$$

where, K_B is the dissociation constant of the base BOH.

It is clear from equation (i) that higher the value of $[H^+]$, the greater the value of K_A. The acidic strength will, thus, be greater. For example, the values of K_A for acetic acid and formic acid are $1 \cdot 8 \times 10^{-5}$ and $1 \cdot 8 \times 10^{-4}$ respectively. Hence, formic acid is stronger than acetic acid.

Similarly, equation (ii) indicates that higher the value of $[OH^-]$, the greater the value of K_B. The basic strength will thus be greater. For example, the values of K_B for NH_4OH and pyridine are $1 \cdot 81 \times 10^{-5}$ and $1 \cdot 30 \times 10^{-9}$ respectively. Hence, the basic strength of NH_4OH is greater than that of pyridine.

K_A for Acids

Acid	Reactions	K_A at 25°C
CH_3COOH	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO-$	1.8×10^{-5}
$HCOOH$	$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO-$	1.8×10^{-6}
HCN	$HCN + H_2O \rightleftharpoons H_3O^+ + CN-$	4.8×10^{-10}
HF	$HF + H_2O \rightleftharpoons H_3O^+ + F-$	6.8×10^{-4}
HNO_2	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2-$	4.5×10^{-4}
H_2CO_3	$CO_2 + 2H_2O \rightleftharpoons H_3O^+ + HCO_3-$	4.3×10^{-7}
H_3PO_4	$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4-$	7.5×10^{-3}

K_B for Bases

Bases	Formula	K_B at 25°C
Ammonia	NH_4OH	1.81×10^{-5}
Dimethlyamine	$(CH_3)_2NH$	5.12×10^{-4}
Ethyl amine	$C_2H_5NH_2$	5.60×10^{-4}
Pyridine	C_5H_5N	1.30×10^{-9}
Urea	$CO(NH_2)_2$	1.50×10^{-14}

2. Strengths of Hydracids (HX) :

The strengths of hydracids depend upon the following factors :
(i) Size of the atom forming the anion.
(ii) Oxidation state of the non-metal.

In $H-X$, as the size of X increases, bond strength decreases, making loss of a proton easier. The order of acidic strength is thus,

$$HF < HCl < HBr < HI$$
$$H_2O < H_2S < H_2Se < H_2Te$$
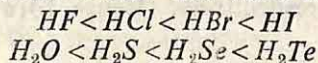
Electronegativity increases appreciably from left to right within a period of the periodic table. Higher the electronegativity of the central atom, greater the acidic strength. Electronegativity of $N <$ that of $O <$ that of F. Hence, the hydrides of monoatomic anions in period 2 have acid strengths in the order

$$NH_3 < H_2O < HF$$
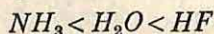
In period 3, we have
$$PH_3 < H_2S < HCl$$

The acidic strength of H_2O_2 is greater than that of H_2O :

$$H_2O_2^{-1} \qquad\qquad H_2O^{-2}$$

The oxygen atoms in H_2O_2 have oxidation states -1 and -2 respectively. The negative charge on oxygen atom in H_2O is thus greater than than that in H_2O_2. Hence, H^+ in H_2O is strongly held to O than H^+ ion in H_2O_2.

$\therefore$ Acidic strength of $H_2O_2 >$ the acidic strength of H_2O.

Strengths of Oxy-acids :

(i) **From the effective charge on O atom**—The charge of the anion in oxy-acids may be regarded as distributed uniformly on all O-atoms. The charge present on an O-atom is called **effective charge.**

Examples :

Acid	anion	effective charge
$HClO$	$(ClO)^{-1}$	-1
$HClO_2$	$(ClO_2)^{-1}$	$-\frac{1}{2}$
$HClO_3$	$(ClO_3)^{-1}$	$-\frac{1}{3}$
$HClO_4$	$(ClO_4)^{-1}$	$-\frac{1}{4}$

The higher value of effective charge indicates a stronger bond between H and O. Hence, in aqueous solution less H^+ ions will be produced. This means, acidic strength will be weak. Thus, in above cases, the order of acidic strength will be.

$$HClO < HClO_2 < HClO_3 < HCl_4$$
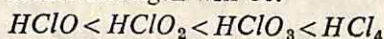
Strengths of Bases :

(A) **Hydra bases :**

(a) Smaller the value of the atomic radius, greater the basic strength of the base.

(b) Smaller the amount of the oxidation state, greater the basic strength of the base.

$\therefore$ ·Basic strength of $NH_3 >$ Basic strength of PH_3
  „   „ $NH_3 >$ „   „ N_2H_4

(B) **Hydroxides,** $M(OH)_x$: (a) Greater the radius of M, the higher the basic strength. Hence,

$$NaOH < KOH < RbOH$$
$$Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$$
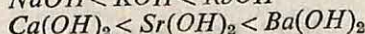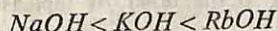
(b) Lower the oxidation number of M, higher the basic strength.

$$NaOH > Ca(OH)_2$$
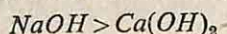
Questions

Long Answer Type :

1. Give a definition of an acid and a base according to the Bronsted-Lowry concept. Give two examples in each case.   (B. U. 1977)

2. Define with suitable examples the terms **acid** and **base** in the light of Lewis electronic concept.

3. Explain why water behaves both as an acid and a base.

4. What do you mean by a **conjugate pair** ?

5. Give a definition and an example of an amphoteric substance. Discuss the cause of amphoterism.

6. Deduce Ostwald's dilution law.

7. Arrange the following acids in the crder of increasing acidic strength : $HClO$, $HClO_2$, H_2SO_4, H_3PO_4, HF and HNO_2.   (B. U. 1974)

8. What is the difference between dissolving HCl and dissolving $NaCl$ in water in terms of the formation of ions ?

9. (a)   What is Lewis's concept of acids and bases ?

   (b)   Classify the reagents in the following reactions among acids and bases :

(i) $$H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: + \overset{\displaystyle F}{\underset{\displaystyle F}{B}}-F \;\rightarrow\; H-\overset{\displaystyle H}{\underset{\displaystyle H}{N}}: \overset{\displaystyle F}{\underset{\displaystyle F}{B}}-F;\quad \text{(ii)}\quad H^+ + H_2\overset{..}{O}: \rightarrow (H_3O^+)$$
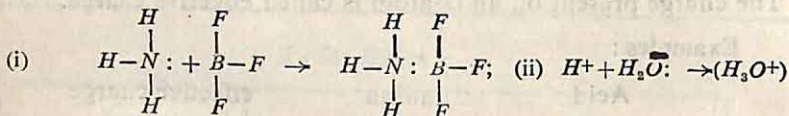
                    (B. U. 1975)

Short Answer Type :

1. Write equations to show the autoionisation of the following substances acting as solvents in acid-base reactions according to the solvent-system concept :

$$H_3PO_4,\ HCOOH,\ H_2N\,C_2H_4\,NH_2$$

2. By means of the Lewis concept, show by electron-dot formulae how each acid-base pair may neutralise each other :

Acid	Base
H^+	O^{--}
BF_3	NH_3
Al^{3+}	H_2O
SO_3	OH^-

3. Give the Lewis definition for an acid.

4. What is a neutralisation reaction in the light of Bronsted-Lowry concept ?

5. Define **acidic oxide** and **basic oxide**.

6. Chose which of the following are acidic and which are basic oxides :
$$SO_2, CaO, P_4O_{10}, N_2O_5, Na_2O$$

7. What do you mean by the pH of a solution ?

8. "Sulphuric acid is a dibasic acid". Explain.   (B. U. 1973)

9. Explain why HF is not as strong an acid as HI even though the electronegativity of fluorine is the highest of all the elements.

10. Arrange the following in the order of increasing acidity (write the weakest acid first) :

$$HOCl,\ HOI,\ HOBr$$ (I.I.T. 1978)

11. State what will happen if to a solution of acetic acid some hydrochloric acid is added.

Numerical Problems :

1. Calculate the concentration of hydrogen ions in 18 g of water.

2. The pH value of a solution is 4. Find the $[H^+]$ and $[OH^-]$ in the solution.

3. What will be the pH of a solution in which $[OH^-]$ at 25°C is 6.6×10^{-5} mole litre^{-1} ?

4. A solution contains 0.18 g of HCl per litre. Assuming complete ionisation of HCl, find the pH of the solution.

5. The dissociation constant of acetic acid is 1.8×10^{-5}. Find the degree of dissociation of acid in a N/10 solution of it.

Objective Questions :

(A) 1. Which of the following is the strongest acid ?
(i) CH_3COOH, (ii) $CH_2Cl\,COOH$, (iii) $CHCl_2COOH$, (iv) CCl_3COOH.

2. Which one of the following is the strongest acid ?
(i) $HClO_4$, (ii) $HBrO_4$, (iii) $HClO_3$, (iv) $HClO_2$

3. An aqueous solution of ferric chloride is
(i) acidic, (ii) alkaline, (iii) neutral, (iv) amphoteric.

4. The decreasing acidic strength of $HClO_4$, $HClO_3$, $HClO_2$, $HClO$ is
(i) $HClO_4 > HClO > HClO_2 > HClO_3$.
(ii) $HClO_2 > HClO > HClO_3 > HClO_4$.
(iii) $HClO_4 > HClO_3 > HClO_2 > HClO$.
(iv) $HClO_3 > HClO_2 > HClO > HClO_4$.

5. Which of the following is the strongest acid ?
(i) $HClO$, (ii) $HBrO$, (iii) HIO, (iv) H_2CO_3.

6. Which of the following is a dibasic acid ?
(i) HCl, (ii) H_2SO_4, (iii) H_3PO_4, (iv) HNO_3.

7. An acid is a substance which has got
(i) pH less than 7,   (ii) pH greater than 7,
(iii) pH equal to 7,   (iv) none of these.

8. According to Arrhenius theory, an acid is defined as a substance which contains
(i) H^+ ions in aqueous solution.
(ii) H_3O^+ ions in aqueous solution.
(iii) OH^- ions in aqueous solution.
(iv) HCl in aqueous solution.

9. According to Bronsted-Lowry concept, an acid is a substance which
(i) accepts protons,   (ii) donates protons,
(iii) accepts electron-pair,   (iv) donates electron-pair.

10. Cu^{++} ion is a
(i) Lewis base,   (ii) Lewis acid,
(iii) metal,   (iv) Bronsted acid.

11. A Lewis base is a substance which can
(i) accept an electron-pair,   (ii) donate an electron-pair,
(iii) donate protons,   (iv) donate H_3O^+ ions,

12. In the reaction, $HBr + H_2O \rightleftharpoons H_3O^+ + Br$, Br^- ion is called
(i) Conjugate acid of HBr,   (ii) Conjugate acid of H_2O,
(iii) Conjugate base of HBr,   (iv) Conjugate base of H_3O^+.

13. Which of the following salts is insoluble in water ?
(i) $CsCl$, (ii) $BaCl_2$, (iii) $CaCl_2$, (iv) $PbCl_2$, (v) $MgCl_2$. **(PMDT 1978)**

14. Potash alum is a
  (i) simple salt,   (ii) complex salt,
  (iii) double salt,   (iv) acid salt.   (PMDT 1976)

15. Which of the following dissolves in water to give a neutral solution ?
  (i) $(NH_4)_2SO_4$,   (ii) $Ba(NO_3)_2$,   (iii) $CrCl_3$,
  (iv) $CaSO_4$,   (v) $NuOH$.   (MDAT 1980)

16. HCl reacts with water according to the equation
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
Here, HCl acts as
  (i) Lewis acid, (ii) Lewis base, (iii) Bronsted acid, (iv) Bronsted base.
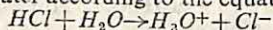
17. In the reaction of NH_3 with water, the latter acts as
  (i) Lewis base,   (ii) Lewis acid,
  (iii) Bronsted base,   (iv) Bronsted acid.

18. The conjugate acid of NH_3 is
  (i) Water,   (ii) HCl,   (iii) NH_4^+,   (iv) OH^-,

19. Which one of the following is a Lewis acid ?
  (i) $AlCl_3$,   (ii) NH_3,   (iii) PH_3,   (iv) Cl^-.

20. Acetic acid is a weak acid because
  (i) its aqueous solution is acidic.
  (ii) it is highly ionised.
  (iii) it is weakly ionised.
  (iv) it contains a $-COOH$ group.

21. Glauber salt is
  (i) acid salt, (ii) mixed salt, (iii) neutral salt, (iv) basic salt.

22. Carnallite is a
  (i) mixed salt, (ii) double salt, (iii) complex salt, (iv) normal salt.

23. Arrangement of NH_3, H_2O, PH_3 in the order of decreasing basicity is
  (i) $NH_3 > PH_3 > H_2O$,   (ii) $NH_3 > H_2O > PH_3$,
  (iii) $PH_3 > NH_3 > H_2O$,   (iv) $H_2O > PH_3 > NH_3$.

24. The order of increasing acidic nature of HI, HNO_3, HNO_2 is
  (i) $HNO_3 > HNO_2 > HI$,   (ii) $HNO_2 > HNO_3 > HI$,
  (iii) $HI > HNO_2 > HNO_3$,   (iv) $HNO_3 > HNO_2 > HI$,

25. The order of increasing acidic nature of NO_2, CO_2, SO_2 is
  (i) $NO_2 < CO_2 < SO_2$,   (ii) $CO_2 < NO_2 < SO_2$,
  (iii) $CO_2 < SO_2 < NO_2$,   (iv) none of these.

26. The order of increasing basic nature of KOH, $Mg(OH)_2$, $NaOH$ is
  (i) $Mg(OH)_2 < NaOH < KOH$,   (ii) $NaOH < Mg(OH)_2 < KOH$,
  (iii) $KOH < NaOH < Mg(OH)_2$,   (iv) $Mg(OH)_2 < KOH < NaOH$.

27. Which of the following is a cationic complex ?
  (i) $K[Ag(CN)_2]$,   (ii) $[Fe(H_2O)_5NO], SO_4$
  (iii) $[Cu(NH_3)_4]SO_4$,   (iv) none of these.

28. A salt containing a higher proportion of the base is known as
  (i) Acidic salt,   (ii) Normal salt,   (iii) Basic salt.

29. The reaction $Pb(OH)_2 + HNO_3 \rightarrow Pb(OH)NO_3 + H_2O$ shows that $Pb(OH)NO_3$ is :
  (i) A base, (ii) An acid, (iii) A basic salt, (iv) An acidic salt.

30. The conjugate base of sulphuric acid is
  (i) sodium hydroxide, (ii) hydrochloric acid, (iii) bisulphate ion, HSO_4^-.

31. A base is a substance which
 (a) accepts protons, (b) donates protons,
 (c) donates electrons, (d) accepts an clectron-pair. **(B. U. 1979)**

32. $H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$
$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{--}$
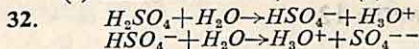
Here HSO_4^- behaves as

(a) an acid, (b) a base,
(c) both as an acid and a base, (d) neither as an acid nor a base.

33. Partial neutralisation of a polybasic acid gives

(i) acid salts, (ii) basic salts, (iii) neutral salts,
(iv) mixed salts, (v) double salts.

34. In the following reaction
 $AlCl_3 + Cl^- \rightarrow AlCl_4^-$,
$AlCl_3$ can be considered to be
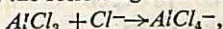
(i) a Lewis acid, (ii) a Lewis base, (iii) a salt,
(iv) a cation, (v) none of these.

35. Strongest base among the following is
 (i) $Mg(OH)_2$, (ii) $Sr(OH)_2$, (iii) $Ca(OH)_2$, (iv) $Ba(OH)_2$.

36. Aluminium hydroxide behaves as

 (i) oxidising agent, (ii) reducing agent,
 (iii) basic substance, (iv) amphoteric substance.

(B) Write **T** for true statement and **F** for false statement in the following :

5. Lewis acids are electrophiles.
6. Na_2SO_4 is an acid salt.
7. An acid is a substance which releases protons.
8. The ionic product of water (K_w) is a constant at all temperatures.
9. The acidic strength depends on the capacity of a substance to furnish hydrogen ions in aqueous solution.

□ □ □

CHEMICAL EQUILIBRIUM

Chemical reactions can be divided into two classes :

(i) **Irreversible** and (ii) **Reversible.**

Irreversible Reactions—Reactions which proceed completely in one direction only are called **irreversible reactions.**

$$2KClO_3 \xrightarrow{heated} 2KCl + 3O_2$$
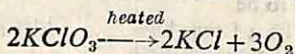
Reversible Reactions—Reactions which proceed in both the forward and the reverse directions appreciably are called **reversible reactions.**

$$H_2 + I_2 \rightleftarrows 2HI$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
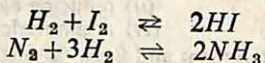
Equilibrium—We know that the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reacting species.

Let us consider the reaction,

$$A + B \rightleftharpoons C + D.$$
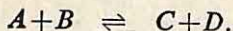
Initially, the molar concentrations of C and D are, nil. When reaction starts, the concentrations of A and B gradually decrease, whereas those of C and D increase. The reverse reaction also starts then. As time passes on, the rate of the forward reaction goes on decreasing, whereas the rate of the reverse reaction goes on increasing. A stage is eventually reached in which the rate of the forward reaction becomes equal to that of the reverse reaction. Under this condition, the composition of the reaction mixture becomes constant and does not change with time. Such a condition of a chemical reaction is called **Chemical Equilibrium.** Thus, **the state of a chemical reaction in which the rate of the forward reaction becomes equal to that of the reverse reaction, is called chemical equilibrium.**

In equilibrium, the reaction appears to have stopped. But this is not so. Reactions in both the directions go on undisturbed, but with equal speed. Hence, a chemical equilibrium is also known as a **Dynamic Equilibrium.**

Characteristics of Chemical equilibrium

(i) In a state of chemical equilibrium the forward and the reverse reactions occur at equal speeds.

(ii) In this state the composition of the reacting mixture becomes fixed, i.e., the concentrations of the reactants and the products do not change with time.

The Law of Mass Action

In 1867, **Guldberge** and **Wage** stated the famous **Law of Mass Action** as follows—

The rate of a chemical reaction is proportional to the product of the active masses of the reactants.

Active Mass—The term active mass may be taken as equal to molar concentration, i.e. number of moles of the reacting substance present per litre. The active mass of a solid is taken as unity.

The Equilibrium Constant

Let us consider the following reversible reaction occurring at a constant temperature :

$$A + B \rightleftharpoons C + D$$

Rate of the forward reaction $\propto [A] \times [B]$

or $\qquad r_1 = k_1 [A] \times [B]$

where K_1 is the proportionality constant, known as the **rate constant** of the forward reaction.

Rate of the reverse reaction $\propto [C] \times [D]$

or $\qquad r_2 = k_2 [C] \times [D]$

where K_2 is the proportionality constant, known as the **rate constant** of the reverse reaction.

At equilibrium, $r_1 = r_2$.

$$\therefore \quad k_1[A] \times [B] = k_2[C] \times [D], \quad \text{or} \quad \frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K_C.$$

K_C is called the **Equilibrium Constant** of the reaction.

The equilibrium constant is, thus, the ratio of the rate constant of the forward reaction to the rate constant of the reverse reaction.

i.e., $$K_C = \frac{k_1}{k_2}.$$

It is a constant for every chemical reaction at a given temperature.

For the reaction, $2A + B \rightleftharpoons C + D$, it is given by,

$$K_C = \frac{[C] \times [D]}{[A]^2 \times [B]}.$$

In general, for the reaction represented by

$$aA + bB \;\rightleftharpoons\; cC + dD,$$
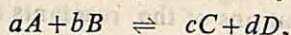
the equilibrium constant will be expressed by

$$K_C = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}.$$

Relation between K_C and K_P :

For gaseous reactions, it is useful to apply **partial pressures** instead of **molar concentrations**. The equilibrium constant is then denoted by K_P.

Let us consider the general gaseous reaction represented by

$$aA + bB \;\rightleftharpoons\; cC + dD$$
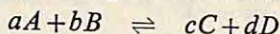
$$K_P = \frac{p_C{}^c \times p_D{}^d}{p_A{}^a \times p_B{}^b}. \qquad \ldots \text{(i)}$$

K_C would be given by the expression

$$K_C = \frac{C_C{}^c \times C_D{}^d}{C_A{}^a \times C_B{}^b}. \qquad \ldots \text{(ii)}$$

p and C stand for partial pressure and molar concentration respectively.

Assuming that the gases behave ideally, we can write

$$pV = nRT; \quad \text{or} \quad p = \left(\frac{n}{V}\right)RT = CRT.$$

$\therefore$ Partial pressure of A, $(p_A) = C_A RT$.
Similarly $p_B = C_B RT$, $p_C = C_C RT$, $p_D = C_D RT$.

$$\Delta \qquad K_P = \frac{(C_C RT)^c \times (C_D RT)^d}{(C_A RT)^a \times (C_B RT)^b}$$

$$= \left(\frac{C_C{}^c \times C_D{}^d}{C_A{}^a \times C_B{}^b}\right) \times \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$= K_C \times (RT)^{(c+d)-(a+b)}$$

$$= K_C \times (RT)^{\Delta x}; \quad [\Delta x = (c+d) - (a+b)]$$

$\Delta x = $ (Number of moles of products) $-$ (Number of moles of reactants).

Thus, when there is no change in the number of moles consequent to a chemical reaction, i.e., when $\Delta x = 0$, then $K_P = K_C$.

Unit of K

The value of K is independent of the molar concentrations of the

reactants and the products but changes only with change in temperature. K has no units, i.e., it is dimensionless if there occurs no change in the number of moles in the reaction. For example, in the reaction

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$
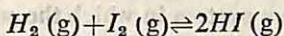
$$K = \frac{[HI]^2}{[H_2] \times [I_2]} = \frac{(\text{mole litre}^{-1})^2}{\text{mole litre}^{-1} \times \text{mole litre}^{-1}} = \frac{(\text{mole litre}^{-1})^2}{(\text{mole litre}^{-1})^2}.$$

But when there is change in the number of moles, K will have units. For example, in the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}.$$
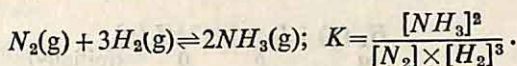
$\therefore$ Unit of $K = \dfrac{(\text{mole litre}^{-1})^2}{\text{mole litre}^{-1} \times (\text{mole litre}^{-1})^3}.$

$\therefore$ Unit of K will be mole^{-2} litre^2.

Usefulness of the Equilibrium Constant (K)—The equilibrium constant is a measure which indicates the extent to which a chemical reaction may occur before the equilibrium is attained.

Example : (i) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$
$K = 1.35 \times 10^{-11}$ mole litre^{-1}.
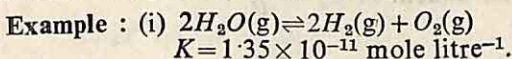
The value of K is very small. Hence, the amounts of H_2 and O_2 will be negligible before the equilibrium is reached. This means that the reverse reaction is almost complete. That is why, a mixture of H_2 and O_2 is dangerously explosive.

(ii) $2O_3(g) \rightleftharpoons 3O_2(g); \quad K = 10^{55}$ mole litre^{-1} at 25°C.
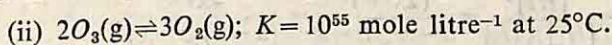
A large value of K indicates that the reaction goes virtually to completion at 25°C.

Types of Chemical Equilibria

There are two types of chemical equilibria :

1. Homogeneous equilibria : In such equilibria, all the reactants and the products are in the same phase.

$$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$$
$$2O_3 (g) \rightleftharpoons 3O_2 (g)$$
$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$
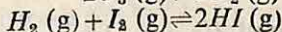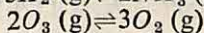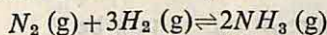
2. Heterogeneous equilibria : In such an equilibria, the reactants and the products are found in two or more phases.

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$$
$$C (s) + H_2O (g) \rightleftharpoons CO (g) + H_2(g)$$
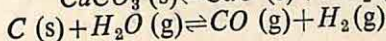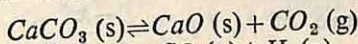
Homogeneous Equilibria

(A) The Gaseous Systems :

Type I : The Gaseous system in which the number of moles remains unchanged.

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2HI \text{ (g)}$$
$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2NO \text{ (g)}$$

Formation of Hydrogen Iodide :

$$\begin{array}{cccc} H_2 \text{ (g)} + & I_2 \text{ (g)} \rightleftharpoons & 2HI \text{ (g)} & \\ a & b & 0 & \text{(initially)} \\ (a-x) & (b-x) & 2x & \text{(at equilibrium)} \end{array}$$
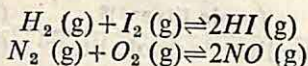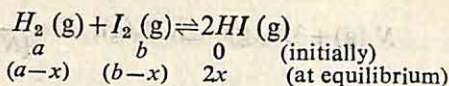
Let a moles of H_2 and b moles of I_2 be present in V litre. At equilibrium, x mole of H_2 and x mole of I_2 combine to form HI.

$$\therefore \quad \text{Equilibrium molar concn. of } H_2 = \frac{a-x}{V}$$

$$\text{Equilibrium molar concn. of } I_2 = \frac{b-x}{V}.$$

$$\text{Equilibrium molar concn. of } HI = \frac{2x}{V}.$$

Applying the Law Mass Action,

$$K_C = \frac{[HI]^2}{[H_2] \times [I_2]} = \frac{(2x/V)^2}{\dfrac{a-x}{V} \times \dfrac{b-x}{V}} = \frac{4x^2}{(a-x)(b-x)}.$$

In terms of **partial pressures**—

$$\begin{array}{cccc} H_2 \text{ (g)} + & I_2 \text{ (g)} \rightleftharpoons & 2HI \text{ (g)} & \\ a \text{ mole} & b \text{ mole} & *0 & \text{(initially)} \\ (a-x) \text{ mole} & (b-x) \text{ mole} & 2x \text{ mole} & \text{(at equilibrium)} \end{array}$$
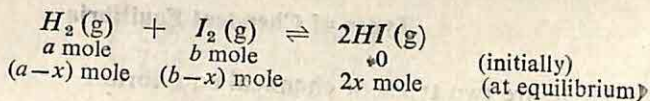
$$\therefore \quad \text{Total number of moles at equilibrium} = a - x + b - x + 2x$$
$$= (a+b).$$

Let the total pressure of the system be P.

$$\therefore \quad \text{Partial pressure of } H_2, \ (p_{H_2}) = \frac{a-x}{a+b} \cdot P$$

$$\text{Partial pressure of } I_2, \ (p_{I_2}) = \frac{b-x}{a+b} \cdot P$$

Partial pressure of HI $(p_{HI}) = \dfrac{2x}{a+b} \cdot P.$

$$\therefore K_P = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}} = \frac{\left(\dfrac{2x}{a+b} \cdot P\right)^2}{\left(\dfrac{a-x}{a+b} \cdot P\right) \times \left(\dfrac{b-x}{a+b} \cdot P\right)}$$

$$= \frac{4x^2}{(a-x)(b-x)}.$$

Thus, $K_P = K_C.$

Formation of Nitric Oxide :

$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2NO \text{ (g)}$$
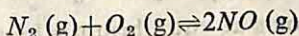
Let a mole of N_2 and b mole of O_2 be present in V litre. Let x mole of N_2 and O_2 each combine to give $2x$ mole of NO at equilibrium. Hence, at equilibrium,

Molar concn. of $N_2 = \dfrac{a-x}{V}$

Molar concn. of $O_2 = \dfrac{b-x}{V}$

Molar concn. of $NO = \dfrac{2x}{V}.$

$$\therefore K_C = \frac{[NO]^2}{[N_2] \times [O_2]} = \frac{(2x/V)^2}{\dfrac{a-x}{V} \cdot \dfrac{b-x}{V}} = \frac{4x^2}{(a-x)(b-x)}.$$

Type II : The Gaseous system in which there is change in the number of moles—

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$
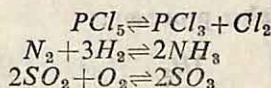
Dissociation of Phosphorus Pentachloride :

PCl_5	$\rightleftharpoons$	PCl_3	$+$	Cl_2	(closed vessel of vol. V)
1 mole		0		0	(initially)
$(1-x)$ mole		x mole		x mole	(at equilibrium)
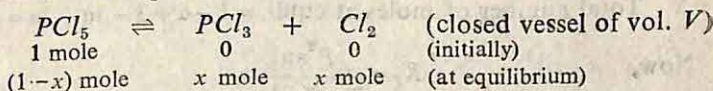
(x is the degree of dissociation of PCl_5)

$$\therefore K_C = \frac{\dfrac{x}{V} \times \dfrac{x}{V}}{\dfrac{1-x}{V}} = \frac{x^2}{(1-x)V}.$$

If the degree of dissociation x is small, then

$$K_C = \frac{x^2}{V}, \quad \text{or} \quad x^2 \propto V$$

or

$$x \propto \sqrt{V}, \quad \text{or} \quad x \propto \sqrt{\frac{1}{P}}.$$

Thus, **the degree of dissociation varies inversely as the square root of pressure of the system.**

In terms of partial pressures :

$$\underset{\substack{1 \\ (1-\alpha)}}{PCl_5} \rightleftharpoons \underset{\substack{0 \\ \alpha}}{PCl_3} + \underset{\substack{0 \\ \alpha}}{Cl_2}$$
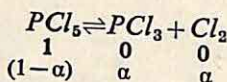
Total number of moles at equilibrium $= 1 - \alpha + \alpha + \alpha = (1 + \alpha)$.
Let the total pressure be P.

$$\therefore \quad p_{PCl_5} = \frac{1-\alpha}{1+\alpha} \cdot P; \quad p_{PCl_3} = \frac{\alpha}{1+\alpha} \cdot P; \quad p_{PCl_3} = \frac{\alpha}{1+\alpha} \cdot P.$$

$$\therefore \quad K_P = \frac{\left(\dfrac{\alpha}{1+\alpha} \cdot P\right)\left(\dfrac{\alpha}{1+\alpha} \cdot P\right)}{\dfrac{1-\alpha}{1+\alpha} \cdot P} = \frac{\alpha^2 P}{1-\alpha^2}.$$

K_P is a constant at a given temperature. Hence, decrease of P will cause increase in α (i.e. degree of dissociation).
If α is very small, then

$$K_P = \alpha^2 P \quad \text{or} \quad \alpha = \sqrt{\frac{K_P}{P}}$$

i.e.. the degree of dissociation varies inversely as the square root of pressure.

Formation of Ammonia (Haber process) :

$$\underset{\substack{1 \text{ mole} \\ (1-\alpha) \text{ mole})}}{N_2} + \underset{\substack{3 \text{ mole} \\ 3 (1-\alpha) \text{ mole}}}{3H_2} \rightleftharpoons \underset{\substack{0 \\ 2\alpha \text{ mole}}}{2NH} \quad \substack{\text{(initially)} \\ \text{(at equilibrium)}}$$
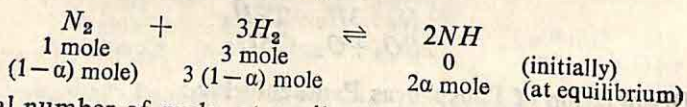
$$\therefore \quad \text{Total number of moles at equil.} = 1 - \alpha + 3 - 3\alpha + 2\alpha = (4 - 2\alpha).$$

Now,

$$K_P = \frac{p^2_{NH_5}}{p_{N_2} \times p^3_{H_2}}$$

Let the total pressure be P. Then,

Partial pressure of NH_3, $p_{NH_3} = \frac{2\alpha}{4 - 2\alpha} \cdot P$

Partial pressure of N_2, $p_{N_2} = \dfrac{1-\alpha}{4-2\alpha} \cdot P$

Partial pressure of H_2, $p_{H_2} = \dfrac{3(1-\alpha)}{4-2\alpha} \cdot P$.

$$\therefore \quad K_P = \dfrac{\left(\dfrac{2\alpha}{4-2\alpha} \cdot P\right)^2}{\left(\dfrac{1-\alpha}{4-2\alpha} \cdot P\right)\left[\dfrac{3(1-\alpha)}{4-2\alpha} P\right]^3} = \dfrac{4\alpha^2(4-2\alpha)^2}{27(1-\alpha)^4 P^2}.$$

If α is small compared to unity, then

$$K_P = \dfrac{64\alpha^2}{27P^2}, \qquad \therefore \quad \alpha^2 = \dfrac{27K_P \cdot P^2}{64}.$$

$\because$ K_P is constant,

$\therefore$ $\alpha^2 \propto P^2$,   or $\alpha \propto P$.

Hence, increase of pressure causes increase in the value of α, i.e. formation of ammonia is favoured.

(B) The Liquid System :

Esterification of Acetic acid—

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initially a b 0 0

At equil. $a-x$ $b-x$ x x
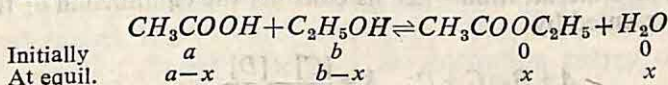
This reaction is brought about in the liquid phase. Let a mole of acetic acid and b mole of ethyl alcohol be mixed together. Let x mole of ethyl acetate be obtained at equilibrium. If V is the total volume of solution, then at equilibrium,

$$[CH_3COOH] = \dfrac{a-x}{V}; \quad [C_2H_5OH] = \dfrac{b-x}{V};$$

$$[CH_3COOC_2H_5] = \dfrac{x}{V}; \qquad [H_2O] = \dfrac{x}{V}.$$

$$\therefore \quad K_C = \dfrac{\dfrac{x}{V} \times \dfrac{x}{V}}{\dfrac{a-x}{V} \cdot \dfrac{b-x}{V}} = \dfrac{x^2}{(a-x)(b-x)}.$$

The equilibrium state is, thus, not affected by change of volume.

Heterogeneous Equilibria

Dissociation of Calcium Carbonate :

$$CaCO_3 \text{ (s)} \rightleftharpoons CaO \text{ (s)} + CO_2 \text{ (g)}$$
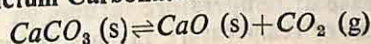
$$K_P = \frac{p_{cao} \times p_{CO_2}}{p_{caco_3}}.$$

The active mass of a solid is assumed to be constant.

$$\therefore \quad K_P = p_{CO_2}.$$

Thus, when $CaCO_3$ is heated in a closed vessel at a given temperature, the pressure of CO_2 becomes constant. This pressure of CO_2 is independent of the amount of $CaCO_3$ used.

Water-gas Reaction :

$$C\ (s) + H_2O\ (g) \rightleftharpoons CO\ (g) + H_2\ (g)$$
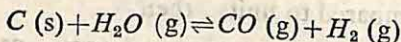
$$K_P = \frac{p_{CO} \times p_{H_2}}{p_C \times p_{H_2 O}}.$$

The partial pressure of carbon is taken as unity. Hence,

$$K_P = \frac{p_{CO} \times p_{H_2}}{p_{H_2 O}}.$$

Factors That Influence Equilibrium

1. Effect of Concentration—Let us consider the equilibrium of the reaction represented by

$$A + B \rightleftharpoons C + D; \quad K = \frac{[C] \times [D]}{[A] \times [B]}.$$
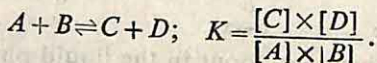
Suppose, some A is added to this equilibrium. The value of $[A]$ is, thus, increased. In order to keep K constant, the concentrations of C and D must increase. Thus, the addition of the reactant results in increasing the concentration of the product, i.e., the forward reaction is favoured.

Similarly, addition of one of the products leads to the formation of the reactants, i.e., the reverse reaction is favoured.

2. Effect of change in temperature—Let us consider the following general reaction :

$$A + B \rightleftharpoons C + D - Q \text{ Kcal}$$
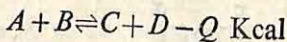
This reaction is **endothermic.** If temperature is increased, the equilibrium shifts in such a way that the heat is absorbed. The formation of the product is, thus, favoured, i.e., more of the product is formed. On the contrary, if the temperature is lowered, the shift in equilibrium occurs in the reverse direction in which the heat is evolved. The reproduction of the reactants is, thus, favoured.

In general, **increase of temperature favours an endothermic reaction, whereas decrease of temperature favours an exothermic reaction.**

3. Effect of pressure—The concentration of the gaseous substances can be altered by changing the pressure. A change in pressure causes a change in volume of the container available to the reacting gases.

Consider the following reaction :

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2NH_3 \text{ (g)}$$
$$\text{1 vol.} \quad \text{3 vol.} \quad \text{2 vol.}$$
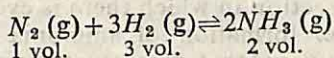
This reaction is accompanied with decrease in volume. Any increase in pressure would cause a decrease in volume. Hence, the equilibrium shifts towards the right. The formation of ammonia is, thus, favoured. Conversely, any decrease in pressure results in the formation of more N_2 and H_2.

Now, consider the following reaction in which the number of moles of the reactants and the products are the same :

$$N_2 \text{ (g)} + O_2 \text{ (g)} \rightleftharpoons 2NO \text{ (g)}$$
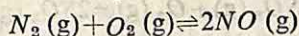
The volume does not change as a result of reaction. Hence, pressure has no effect on the equilibrium of this reaction.

4. Effect of catalyst—At equilibrium, the catalyst increases the rates of both the forward and the reverse reactions to the same extent. The catalyst does not cause any change in the relative amounts present at equilibrium. Hence, the value of the equilibrium constant does not change. The equilibrium is, however, established more rapidly in presence of a catalyst. This is due to the fact that the use of a catalyst decreases the activation energy of both the forward and the reverse reactions.

Le Chatelier's Principle

As a result of studies of the effect of pressure, temperature and concentration on the equilibria of a large number of chemical reactions, Le Chatelier summed up his observations in the form of a principle. This is stated as :

If a system in equilibrium is subjected to a stress, the equilibrium gets shifted in the direction in which the effect of the stress is nullified as far as possible.

Application of Le Chatelier's principle—

1. Synthesis of Ammonia (Haber process) :

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2NH_3 \text{ (g)} + 92 \cdot 38 \text{ KJ}$$
$$\text{1 vol.} \quad \text{3 vol.} \quad \text{2 vol.}$$
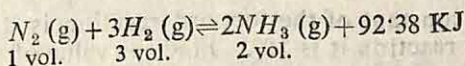
This reaction is exothermic and is attended with decrease in volume. Hence, according to Le Chatelier's principle, increase in pressure shifts the equilibrium in the direction in which there is

decrease in volume. The formation of NH_3 is thus favoured. The higher the pressure, the greater is the yield of ammonia. It is due to this that a pressure of 200 atmosphere is applied.

The reaction is accompanied with evolution of heat. According to the Le Chatelier's principle, lowering of temperature will shift the equilibrium in the direction in which there is evolution of heat. The forward reaction, i.e. formation of ammonia is favoured at lower temperatures. But at very low temperature the rate of reaction may be considerably decreased. In order to overcome this difficulty a catalyst is used and an optimum temperature is maintained. A temperature close to 500°C has been found to be suitable. Finely divided iron is used as a catalyst.

2. Formation of Sulphur trioxide :

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$
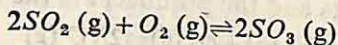
The reaction is accompanied by decrease in volume. According to Le Chatelier's principle, a high pressure would give a better yield of Sulphur trioxide.

The reaction is also exothermic. According to Le Chatelier's principle, therefore, a better yield of sulphur trioxide is expected at very low temperature. The optimum temperature in this case is about 450°C. Platinised platinum is used as a catalyst to hasten the attainment of equilibrium.

3. Formation of Nitric Oxide :

$$N_2 + O_2 \rightleftharpoons 2NO - 44 \text{ Kcal.}$$
$$\text{1 vol. 1 vol. 2 vol.}$$
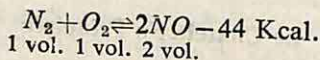
The reaction is endothermic, i.e. it occurs with the absorption of heat. According to Le Chatelier's principle, increase in temperature will shift the equilibrium in the direction in which heat is absorbed. The forward reaction, i.e., formation of Nitric oxide is, thus, favoured at high temperature. This reaction is actually carried out at the temperature of the electric-arc (about 3000°C).

The reaction suffers no volume-change. Hence, change in pressur does not cause any change in the equilibrium of this reaction.

Solved Problems

1. The rate constant of the forward reaction is 10^4, while that of the reverse reaction it is 10^6. Find the value of the equilibrium constant.

(B. U. 1978)

Solution : Rate constant of the forward reaction, $k_1 = 10^4$
Rate constant of the reverse reaction, $k_2 = 10^6$

$$\therefore \quad \text{Equilibrium constant, } K = \frac{k_1}{k_2} = \frac{10^4}{10^6} = 10^{-2}.$$

2. The value of K_P for the equlibrium :

$$2H_2O \text{ (g)} + 2Cl_2 \text{ (g)} \rightleftharpoons 4HCl \text{ (g)} + O_2 \text{ (g)}$$
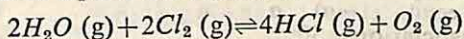
is 0·035 atmosphere at 400°C when the partial pressures are expressed in atmospheres. Calculate the value of K_C for the same reaction.

Solution : $\qquad K_P = K_C(RT)^{\Delta x}$
In this reaction, $\triangle x = (4+1) - (2+2) = 1$
$$K_P = 0·035$$

$$\therefore \quad 0·035 = K_C(0·082 \times 673)^1$$

$$\therefore \quad K_C = \frac{0·035}{0·082 \times 673} = 6·342 \times 10^{-4} \text{ mole litre}^{-1}.$$

3. If 1 mole of H_2O and 1 mole of CO are taken in a 10 litre flask and heated to 986°C, 40% of water reacts with carbon monoxide according to the equation :

$$H_2O \text{ (g)} + CO \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + CO_2 \text{ (g)}$$

Calculate the equilibrium constant K for the reaction.
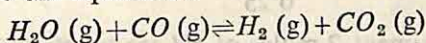
Solution : $\quad H_2O \text{ (g)} + CO \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + CO_2 \text{ (g)}$
Initially : $\quad$ 1 mole $\quad$ 1 mole $\qquad$ 0 $\qquad$ 0
At equil. : $\quad$ (1−0·4) (1−0·4) $\quad$ 0·4 mole 0·4 mole
$\qquad$ = 0·6 mole = 0·6 mole

Conc. at equil. : $\dfrac{0·6}{10} = 0·06, \dfrac{0·6}{10} = 0·06, \dfrac{0·4}{10} = 0·04, \dfrac{0·4}{10} = 0·04.$

Now, $\quad K = \dfrac{[H_2] \times [CO_2]}{[H_2O] \times [CO]} = \dfrac{0·04 \times 0·04}{0·06 \times 0·06} = \dfrac{4 \times 4}{6 \times 6} = 0·44.$

4. When 1 mole of acetic acid and 1 mole of ethyl alcohol react together, 2/3 mole of ethyl acetate is formed at equilibrium. Calculate the equilibrium constant of the reaction.
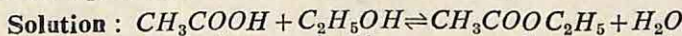
Solution : $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
Initially $\quad$: $\quad a$ mole $\qquad b$ mole $\qquad$ 0 $\qquad$ 0
At equil. $\quad$: $\quad (a-x) \qquad (b-x) \qquad x \qquad x$

$$K = \frac{x^2}{(a-x)(b-x)} = 4.$$

Here, $\qquad a = 1, \qquad b = 1, \qquad x = 2/3.$

$$\therefore \quad K = \frac{2/3 \times 2/3}{(1-2/3)(1-2/3)} = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = 4.$$

5. Calculate the pressure required for 50% dissociation of PCl_5

at $250°C$. The value of the equilibrium constant K for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, is 1.8.

Solution :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initially 1 0 0

At equil. $(1-\alpha)$ α α

Here,   dissociation $= 50\%$

$$\therefore \quad \alpha = 0.5$$
$$K_P = 1.8.$$
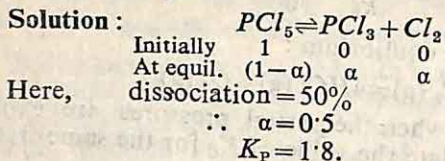
Now,

$$K_P = \frac{\alpha^2 P}{1 - \alpha^2}, \text{ where } P = \text{Total pressure.}$$

$$\therefore \quad 1.8 = \frac{0.5 \times 0.5 \times P}{[1 - (0.5)^2]}$$

or

$$P = \frac{1.8 \times [1 - (0.5)^2]}{0.5 \times 0.5}$$

$$= \frac{1.8 \times 0.75}{0.25} = 5.4 \text{ atm.}$$

6. In an experiment 2 moles of HI are taken into a 5.0 litre container. At $444°C$, K equals to 0.0156 for the gaseous reaction :

$$2HI \text{ (g)} \rightleftharpoons H_2 \text{ (g)} + I_2 \text{ (g)}$$
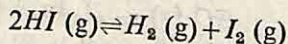
Calculate the equilibrium concentrations of HI, H_2 and I_2. What is the fraction of HI which decomposes ?

Solution :

$$2HI \rightleftharpoons H_2 + I_2$$

$$2 \qquad 0 \quad\ 0$$

$$(2-2x) \quad x \quad\ x$$
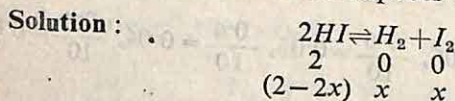
Let $2x$ be the number of moles of HI which decomposes. Hence, according to the above equation, x moles of each H_2 and I_2 will be formed.

$$\therefore \quad \text{Molar concn. of } HI = \frac{2-2x}{5}$$

$$\text{Molar concn. of } H_2 = \frac{x}{5}$$

$$\text{Molar concn. of } I_2 = \frac{x}{5}$$

$$\therefore \quad \text{At equilibrium, } K = \frac{(x/5) \times (x/5)}{\left(\dfrac{2-2x}{5}\right)^2}$$

or $0.0156 = \dfrac{x^2}{25} \times \dfrac{5 \times 5}{(2-2x)^2}$;   or $0.0156 = \dfrac{x^2}{(2-2x)^2}$

or $\dfrac{x}{2-2x} = \sqrt{0.0156} = 0.125$;   or $x = 0.125(2-2x)$

or $1.25x = 0.25$;   or $x = \dfrac{0.25}{1.25} = 0.20$.

∴   Number of moles of $H_2 = x = 0.2$
        Number of moles of $I_2 = x = 0.2$
        Number of moles of $HI = 2 - 2x = 1.60$.
∴   Equilibrium concentrations are :

$$[H_2] = \dfrac{0.2}{5} = 0.04 \text{ mole litre}^{-1}.$$

$$[I_2] = \dfrac{0.2}{5} = 0.04 \text{ mole litre}^{-1}.$$

$$[HI] = \dfrac{1.6}{5} = 0.32 \text{ mole litre}^{-1}.$$

Fraction of HI decomposed $= \dfrac{2x}{2} = x = 0.2$.

∴   % decomposition $= 20\%$.

7. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, the concentrations of H_2, I_2 and HI at equilibrium are 9·6, 2·6 and 30·8 mole litre^{-1} respectively. Find the value of the equilibrium constant.

Solution : $H_2 + I_2 \rightleftharpoons 2HI$
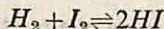
$$K = \dfrac{[HI]^2}{[H_2][I_2]} = \dfrac{(30.8)^2}{9.6 \times 2.6} = 38.$$

8. The equilibrium constant of the reaction,

$$N_2 + O_2 \rightleftharpoons 2NO$$
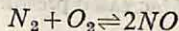
at high temperature is found to be 6.0×10^{-4}. If the concentration of N_2 is 0·1 mole litre^{-1} and that of O_2 is 0·02 mole litre^{-1}, what is the concentration of nitric oxide at equilibrium ?

Solution : $N_2 + O_2 \rightleftharpoons 2NO$
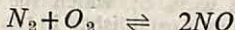
$$K = \dfrac{[NO]^2}{[N_2][O_2]}; \qquad ∴ \quad 6.0 \times 10^{-4} = \dfrac{[NO]^2}{0.1 \times 0.02}$$

or $[NO]^2 = 6.0 \times 10^{-4} \times 0.1 \times 0.02$
∴ $[NO] = \sqrt{6.0 \times 10^{-4} \times 0.1 \times 0.02}$ mole litre^{-1}
        $= 1.08 \times 10^{-3}$ mole litre^{-1}.

9. Assuming that the degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0·15. Calculate the pressure at which this substance will be one-fourth dissociated at the same temperature.

Solution : PCl_5 dissociates as

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$
$$1 - \alpha \qquad\quad \alpha \qquad \alpha$$
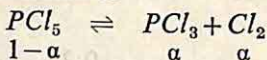
where α = degree of dissociation.

$$\therefore \quad K_p = \frac{\alpha^2 P}{(1 - \alpha^2)}.$$

Here, $P = 1$ atm. and $\alpha = 0·15$

$$\therefore \quad K_P = \frac{0·15 \times 0·15 \times 1}{1 - (0·15)^2} = \frac{0·15 \times 0·15}{(1 - 0·0225)} = 0·023.$$

Let the pressure required for one-fourth dissociation of PCl_5 be P.

Now, $\quad \alpha = 0·25.$ $\qquad \therefore \quad K_P = \frac{\alpha^2 P}{1 - \alpha^2}$

or $\qquad\qquad 0·023 = \frac{0·25 \times 0·25 \times P}{1 - (0·25)^2}$

or $\qquad\qquad P = \frac{0·023 \times 0·9375}{0·25 \times 0·25} = 0·345$ atm.

Questions

Long Answer Type :

1. What is equilibrium condition of a reaction ? Discuss the factors which alter the state of equilibrium.

2. Write short notes on

(i) Le Chatelier's principle, (ii) Equilibrium constant, (iii) State of equilibrium, (iv) Relation between K_P and K_C. (M. U. 1977 A).

3. What will be the effect of increased pressure on the following equilibria ?

(i) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.
(ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.
(iii) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$.
(iv) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

4. Mention at least three ways by which the concentration of SO_2 can be increased, after the equilibrium is established in the following reaction :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3 + 45·2 \text{ Kcal}.$$
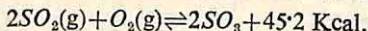
5. Predict the effect of (i) decrease in temperature and (ii) increase in temperature, on each of the following reactions :

(a) $H_2O(g) + \text{heat} \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$
(b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + \text{heat}$
(c) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + \text{heat}.$

6. Establish a relationship between K_P and K_C of a reaction.

7. State the Law of Mass Action. What do you mean by the concentration of a substance ? (I. S. C. Delhi 1978)

8. The manufacture of Nitric Oxide in Birkeland-Eyde process takes place according to the following equation :

$$N_2 + O_2 \rightleftharpoons 2NO - 43 \cdot 2 \text{ Kcal.}$$
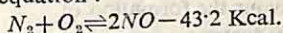
What will be the effect of (i) temperature (ii) pressure and (iii) addition of Oxygen, on the equilibrium of this reaction ? (I. S. C. Delhi 1979)

9. The manufacture of Ammonia by Haber Process is based on the following equilibrium :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + Q \text{ Kcal}$$
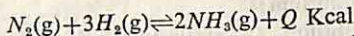
Mention the effect of pressure and temperature on this reaction.

Short Answer Type :

1. What is rate constant of a reaction ?

2. Why is chemical equilibrium referred to as 'dynamic equilibrium' ?

3. From the following data at 25°C, select (a) the most stable and (b) the least stable oxide of nitrogen :

 (i) $2NO_2(g) \rightleftharpoons N_2(g) + 2O_2(g)$; $K = 6 \cdot 7 \times 10^{16}$ mole litre^{-1}.
 (ii) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$; $K = 2 \cdot 2 \times 10^{30}$ mole litre^{-1}.
 (iii) $2N_2O(g) \rightleftharpoons 2N_2(g) + O_2(g)$ $K = 3 \cdot 5 \times 10^{33}$ mole litre^{-1}.
 (iv) $2N_2O_5(g) \rightleftharpoons 2N_2(g) + 5O_2(g)$; $K = 1 \cdot 2 \times 10^{34}$ mole litre^{-1}.
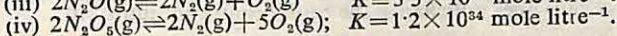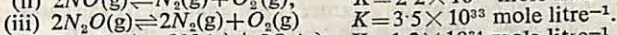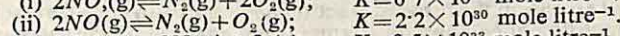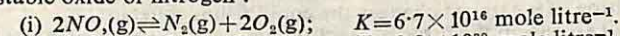
4. What is a reversible reaction ?

5. Write the equations of two reversible reactions in which $K_P = K_C$.

6. Write equilibrium reaction for the following :

$$K = \frac{(p_{N_2})^{\frac{1}{2}} \times (p_{H_2})^{\frac{3}{2}}}{p_{NH_3}}$$

 (ii) $K = \dfrac{[CaCl_2]}{[Ca(OH)_2] \times [HCl]^2}$. (Mithila U. 1978A)

7. Discuss the significance of the 'Equilibrium constant.

8. How is the equilibrium constant of a reaction related to the rate constants of the forward and the reverse reactions ?

Objective Questions :

(A). 1. At equilibrium
(a) the reaction comes to a stop.
(b) the rate of reaction is enhanced.
(c) the rate of the forward reaction increases.
(d) the rate of the forward reaction is counterbalanced by that of the reverse reaction.

2. The value of K_P is equal to that of K_C in the reaction
 (a) $H_2 + I_2 \rightleftharpoons 2HI$, (b) $2SO_2 + O_2 \rightleftharpoons 2SO_3$,
 (c) $N_2 + 3H_2 \rightleftharpoons 2NH_3$, (d) $CaCO_3 \rightleftharpoons CaO + CO_2$.
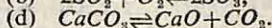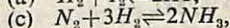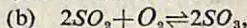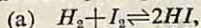
3. The expression for the equilibrium constant of the reaction $2A + 3B \rightleftharpoons aC$ is

 (a) $-\dfrac{[C]}{[A] \times [B]}$, (b) $\dfrac{[C]^a}{[A]^3 \times [B]^3}$, (c) $\dfrac{a[C]}{[A]^3 \times [B]^2}$, (d) $\dfrac{a[C]}{[A] \times [B]}$.

4. In the synthesis of NH_3 by Haber's process, increase in pressure at equilibrium
(a) increases the yield of NH_3, (b) reduces the yield of NH_3, (c) has no effect on the yield of NH_3, (d) converts the reactants and products into liquid.
              (P.M.D.T. Bihar, 1976)

5. In which of the following reactions is the formation of products favoured at low pressure ?

(a) $N_2+3H_2 \rightleftharpoons 2NH_3$, (b) $2SO_2+O_2 \rightleftharpoons 2SO_3$, (c) $PCl_5 \rightleftharpoons PCl_3+Cl_2$.
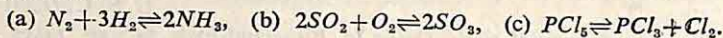
6. According to Le Chatelier's principle, application of high pressure to the reaction $H_2+I_2 \rightleftharpoons 2HI$ will favour the formation of

(a) reactants, (b) products, (c) none. **(P.M.D.T. Bihar 1977)**

7. The catalyst used in the manufacture of NH_3 by Haber's process is

(a) Mg, (b) Pt, (c) Fe, (d) Mo. **(A.F.M.C. Pune, 1973)**

8. The chemical equilibrium is

(a) dynamic equilibrium, (b) static equilibrium, (c) physical equilibrium.

9. The function of a catalyst is to

(a) change equilibrium, (b) increase the yield of the product, (c) change the rate of reaction.

(B) Select the correct statement from the following :

1. The addition of a catalyst changes the equilibrium constant.
2. A catalyst speeds up the forward reaction and retards the reverse reaction.
3. The composition of equilibrium mixture is not changed by the catalyst.
4. Pressure change does not change the equilibrium concentration.

Numerical Problems :

1. For the dissociation of water, $H_2O \rightleftharpoons H_2(g)+\frac{1}{2}O_2(g)$, at 1500°C, the value of K_P with partial pressure in atmosphere is 1.87×10^{-6} Assuming ideal behaviour of gases, calculate the value of K_C with concentrations in mole litre^{-1}.

(Ans. 1.55×10^{-7} mole litre^{-1})

2. 15 moles of Hydrogen, on interacion with 5.2 moles of Iodine vapours at 444°C produced 10 moles of Hydrogen iodide. Determine the equilibrium constant of the reaction. (Ans. 50)

3. For the reaction $A+B \rightleftharpoons C+D$, $p_A=0.40$ atm., $p_B=0.30$ atm., $p_C=0.20$ atom, and $p_D=0.10$ atm. Calculate K_P. (Ans. 0.17).

4. 1 mole of Ethyl alcohol is allowed to react with 4 moles of Acetic acid. 0.933 mole of Ethyl acetate was formed at equilibrium. Calculate the equilibrium constant. (Ans. 4.236)

5. The dissociation of N_2O_4 into NO_2 at 70°C and atmospheric pressure was found to be 60%. Under this condition, what will be the volume of 10 g of N_2O_4 ? **(M.U. 1974 A)** (Ans. 5.07 litre)

6. The degree of dissociation of N_2O_4 at 53°C and 783.3 mm. pressure is 0.448. Calculate the values of K_P and K_C.

(Ans. $K_P=3.49 \times 10^{-2}$; $K_C=6.1 \times 10^{-4}$)

7. The equilibrium partial pressures of SO_2, O_2 and SO_3 are 0.309, 0.353 and 0.338 atmospheres respectively. Calculate the equilibrium constant for the following reaction :
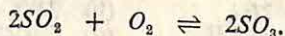
$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$ (Ans. 3.4)

8. If the equilibrium concentrations of H_2, I_2 and HI for the reaction $H_2+I_2 \rightleftharpoons 2HI$ are 9.6, 2.6 and 30.8 mole litre^{-1}, calculate the equilibrium constant. (Ans. 38)

□□□

CHEMICAL KINETICS

Different chemical reactions take place at different rates. On this basis the reaction may be broadly divided into three parts :

(i) **Fast reactions**—Some of the reactions occur with such rapidity that their rates can hardly be measured. For instance, explosions and various ionic reactions are almost instantaneous.

$$Na^+ + Cl^- \rightarrow NaCl \qquad \text{(instantaneous)}$$
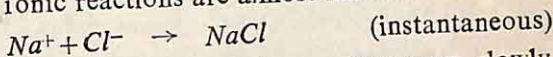
(ii) **Slow reactions**—Some of the reactions occur very slowly and require months or even years to measure their rates. But such a remarkable tolerance on the part of a laboratory worker is unthinkable. For example, combination between hydrogen and oxygen to form water in the absence of a catalyst. This reaction occurs so slowly that it takes years for the formation of even a trace of water.

(iii) **Intermediate reactions**—In between the above two extremes, there are reactions involving both organic and inorganic substances whose rates can well be measured at a desired temperature.

It is only the intermediate reactions with which the study of chemical kinetics is concerned.

The overall reactions does not tell us about the slowness, fastness and the rate of a chemical reaction. It also does not tell how the reaction occurs. That is, the overall reaction fails to tell the mechanism of the reaction, i.e., whether the reaction occurs in one step or in several steps. It is here that 'chemical kinetics' comes to the rescue.

Chemical kinetics is that branch of chemistry which deals with the study of rate and mechanism of chemical reactions.

Rate of Reaction

The rate or velocity of a chemical reaction is defined as the rate at which concentrations of reacting species change (decrease or increase) with time. That is,

$$\text{rate} = \frac{dc}{dt}$$

where, c is the concentration of any reacting substance, and t is the time.

If the concentration of the reacting species decreases with time,

rate $= -\dfrac{dc}{dt}$ but if the concentration increases with time, rate $= +\dfrac{dc}{dt}$.

Example : $$A + B \rightarrow AB$$
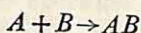
The rate of this reaction may be expressed in terms of rate of change of concentration of any of the reacting species.   Thus,

$$\text{rate of disappearance of } A = -\frac{d[A]}{dt}$$

$$\text{rate of disappearance of } B = -\frac{d[B]}{dt}$$

$$\text{rate of appearance of } AB = +\frac{d[AB]}{dt}.$$

$[A]$, $[B]$ and $[AB]$ are the concentrations of A, B and AB respectively.

The Rate Law :

The rate of reaction is expressed either as a function of the concentration of the reactants or that of the products.   It is, therefore, necessary to find out the species which are involved in the rate. **The expression which determines the rate of reaction as a function of the concentration of each of the substances affecting the rate is known as the rate law or the rate equation for the reaction.**

Let us consider the following reaction :

$$A + B \quad \rightarrow \quad AB$$

If it is experimentally found that the rate of reaction is proportional to the first power of the concentration of A and is independent of the concentration of B, then the rate law will be

$$-\frac{d[A]}{dt} = k[A]^1$$

where k is a constant known as the **rate constant** for the reaction.

The reaction is said to be of the **first order** with respect to A.

If it is found that the rate is proportional to the first power of the concentrations of both A and B, then the rate law will be

$$-\frac{d[A]}{dt} = k[A]^1[B]^1.$$

This reaction is said to be the **first order** with respect to A as well as with respect to B.   The overall order $= 1 + 1 = 2$, i.e., the reaction is of the second order.

Rate determining step—A given reaction may occur through a series of steps. The rates corresponding to different steps may be different. So, the rate of the overall reaction is determined by the step which takes place at the slowest rate. Suppose that the reaction (X) takes place in two steps :

$$2A + B \rightarrow \text{products} \qquad .. \ (X)$$

The first step is $\qquad A + B \rightarrow AB \ (\text{fast}) \qquad .. \ (a)$

The second step is $AB + A \rightarrow \text{products (slow)} \qquad .. \ (b)$
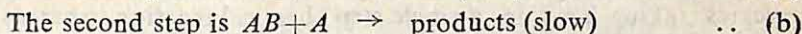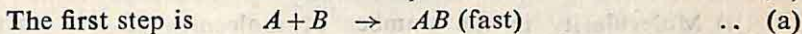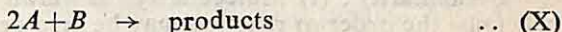
The observed rate of reaction is then equal to the rate of the second step. The second step is, thus, the **rate determining step** of the overall reaction.

The rate is expressed in terms of the concentration of reactants.

$\therefore$ Rate $= k[AB] \ [A]$, ($k =$ rate constant of the reaction).

Now, from the first step (a) :

$$K = \frac{[AB]}{[A][B]}.$$

where, K is the equilibrium constant of the reaction.

$\therefore \ [AB] = K \ [A][B]$. $\therefore$ Rate $= kK[A]^2[B] = K'[A]^2[B]$, $(K' = kK)$.

Relation between the rate constants :

Consider the reaction

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightarrow & 2NH_3 \\ \text{1 mole} & & \text{3 moles} & & \text{2 moles} \end{array}$$
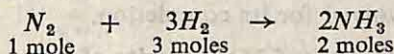
We see that 1 mole of N_2 combines with 3 moles of H_2 to yield 2 moles of NH_3. Thus, the rate of formation of ammonia is twice the rate of disappearance of nitrogen.

Rate of formation of NH_3, $+\dfrac{d[NH_3]}{dt} = k_1[N_2][H_2]^3$

Rate of disappearance of N_2, $-\dfrac{d[N_2]}{dt} = k_2[N_2][H_2]^3$

Rate of disappearance of H_2, $-\dfrac{d[H_2]}{dt} = k_3[N_2][H_2]^3$

k_1, k_2 and k_3 are rate constants.

Now, $-\dfrac{d[H_2]}{dt} = -3\dfrac{d[N_2]}{dt}$ and, $-\dfrac{d[H_2]}{dt} = \dfrac{3}{2}\dfrac{d[NH_3]}{dt}$.

$\therefore \ k_3[N_2][H_2]^3 = 3k_2[N_2][H_2]^3$, or $k_3 = 3k_2$.

Again, $k_3[N_2][H_2]^3 = \dfrac{3}{2}k_1[N_2][H_2]^3$

or $k_3 = \dfrac{3}{2}k_1$ i.e., $\dfrac{3}{2}k_1 = k_3 = 3k_2$.

Difference between Order of Reaction and Molecularity :

Similarity : (i) The value of both does not exceed 3.

(ii) The value of both depends on the condition of reaction.

Dissimilarity : (i) Molecularity is always a whole number, whereas the order of reaction may be zero or fractional.

(ii) Molecularity is the number of molecules of the reacting species taking part in a single step chemical reaction, whereas the order of reaction is the sum of exponents of the molar concentration of the reactants in the rate equation of a chemical reaction, e.g., in a reaction,

$$aA + bB \rightarrow C$$
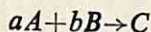
the rate of disappearance of A or B or the rate of formation of C is proportional to the power of concentration of A and B, i.e.,

$$\text{rate} \propto [A]^x \times [B]^y = K[A]^x[B]^y$$

The numerical values of exponents x and y are determined experimentally. x and y may not be necessarily equal to a and b respectively. The sum of the powers of the concentration terms $(x+y)$ in the rate equation is known as the order of reaction. y is the order with respect to B and x is the order with respect to A.

(iii) The molecularity pertains to one single step of the reaction which takes place in a number of steps for its completion, but the order of reaction pertains to reaction as a whole irrespective of the number of steps involved for its completion.

Difference between Order and Molecularity of a Reaction :

Order	Molecularity
1. The order of a reaction is the sum of exponents of the molar concentrations of the reactants which determine the rate of the reaction.	1. The molecularity of a reaction is the number of atoms or molecules of the reactants which actually participate in a single step of the reaction.
2. The order may or may not have relation with the stoichiometric equation representing the reaction.	2. It is calculated from the stoichiometric equation of the reaction.
3. The order pertains to the overall reaction, irrespective of the steps involved for the completion of the reaction.	3. The molecularity pertains to one single step of the reaction which occurs in a number of steps for its completion.
4. It may be a whole number or fractional.	4. It is always a whole number.
5. It is obtained experimentally and not from the balanced chemical equation for the reaction.	5. It is calculated from the single step balanced chemical equation.

First Order Reaction

A reaction is s.id to be of the first order when the rate of this reaction is directly proportional to the concentration of the reactant.

Consider such a reaction represented by,

$$A \rightarrow \text{prodncts.}$$
$$a$$
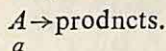
Let a mole litre^{-1} be the initial concentration of the reactant. After time t, let x mole litre^{-1} of A decomposes into the products. Hence, concentration of A left at time $t = (a-x)$ mole litre^{-1}.

∴ Rate of reaction, $\dfrac{dx}{dt} = k_1 (a-x)$

or $\qquad \dfrac{dx}{a-x} = k_1 dt,$ or $\displaystyle\int \dfrac{dx}{a-x} = \int k_1 dt$

or $\qquad -\ln(a-x) = k_1 t + C$

where C is the constant of integration.

When $t = 0$, $x = 0$; ∴ $-\ln a = C$.

Putting the value of C in the above equation, we get,

$$-\ln(a-x) = k_1 t - \ln a, \qquad \text{or} \qquad \ln \frac{a}{a-x} = k_1 t$$

or $\qquad k_1 = \dfrac{1}{t} \ln \dfrac{a}{a-x},$ or $\qquad k_1 = \dfrac{2 \cdot 303}{t} \log \dfrac{a}{a-x}.$

This equation is known as the **Kinetic equation** for a reaction of the first order.

Half-life of a reaction :

The time required for a reaction to be half completed is called half-life period or simply half-life of a reaction.

At the end of the half-life period, the initial concentration (a) of the reactant becomes $a/2$. Let the half-life be denoted by $t_{1/2}$. Then,

$$k_1 = \frac{2 \cdot 303}{t_{1/2}} \log \frac{a}{a-a/2} = \frac{2 \cdot 303}{t_{1/2}} \log 2, \quad \text{or} \quad t_{1/2} = \frac{0 \cdot 693}{k_1}.$$

It follows, therefore, that **the half-life of a reaction is independent of the initial concentration of the reactant.**

Factors Affecting the Rate of Reaction

The rate of a reaction is found to be influenced by several factors. Some of the important factors are :

1. Nature of the reactants.
2. Concentration of the reactants.

3. Temperature.
4. Catalyst.
5. Radiation.

Nature of the Reactants :

Substances differ in chemical activity. For example, the active metals like sodium displace hydrogen from evater even in the cold, but less reactive metal, iron, decomposes only super-heated steam.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 \quad \text{(at ordinary temp.)}$$
$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad \text{(iron should be red hot)}$$

super-heated
steam
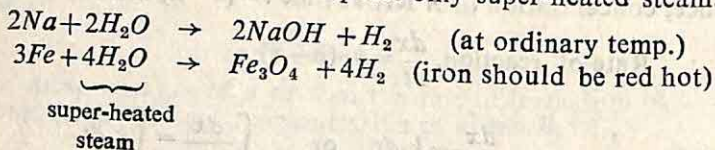
The rate of reaction thus depends heavily on the nature of the reactants.

The reduction of permanganate ion (MnO_4^-) in acid medium by Fe^{++} ion takes place instantaneously, but the reduction of MnO_4^- is slow with oxalate ion $(C_2O_4^{--})$. In these cases, everything is[a] the same except the nature of the reducing agents, i.e., Fe^{++} and $C_2O_4^{--}$ ions. But the reaction rates are quite different.

The above differences in the rates of reactions are due to differences in activation energy. The amount of activation energy is different for different reacting species. The following example will make the point more clear—

$$\text{(i)} \quad NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \quad \text{(fast)}$$
$$\text{(ii)} \quad CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \quad \text{(slow)}$$
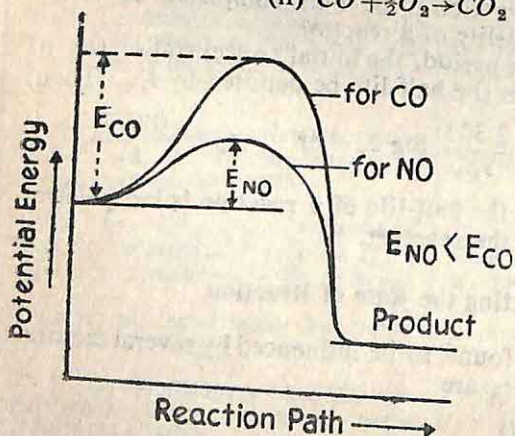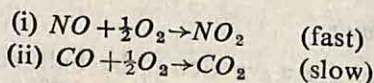
Though both NO and CO molecules are alike still the reaction (i) is fast whereas (ii) is slow. This is so because in the former case the activation energy is low, whereas in the latter it is high (see the given figure).

Concentration of the Reactants :

The rate of a reaction is expressed in terms of the molar concentrations of the reactants. Thus,

$$-\frac{d[A]}{dt} = k[A][B].$$

Any increase in $[A]$ or $[B]$ will increase the rate of reaction. As a rule, the rate of a chemical reaction is proportional to the concentrations of the reacting species. We known that greater the concentrations of the reactant molcules per litre larger will be the number of collisions between the reacting molecules per litre per second. The rate of reaction is thus enhanced.

Temperature :

The temperature has a marked effect on the rate of a chemical reaction. In general, higher the temperature of the reactants, more rapid will be the rate of reaction. It has been estimated that every $10°$ rise in temperature roughly doubles the rate of reaction, and the rate constant, i.e.,

$$\frac{K_{t+10}}{K_t} \approx 10.$$

Arrhenius showed that most reactions follow the equation,

$$\log k = A - \frac{B}{T}$$

where k is the rate constant, T the kelvin temperature, A and B are positive constants.

A plot of $\log k$ against $\frac{1}{T}$ should give a straight line with intercept $= A'$ and slope $= -B$.

We may write the above equation as

$$k = Ae^{-B/T}.$$
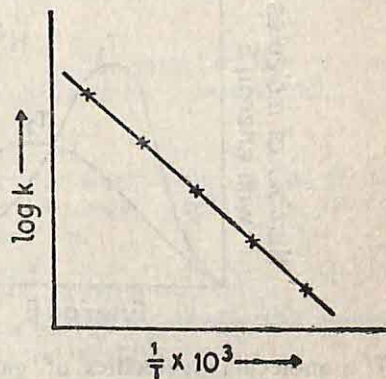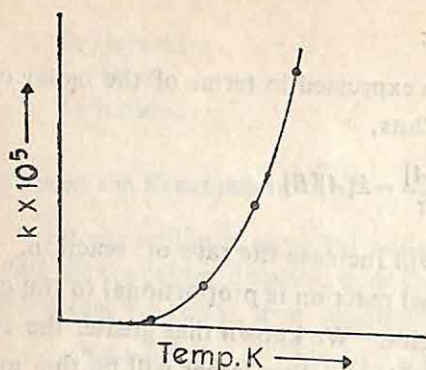
The rate constant k will, thus, increase exponentially with increase in T.

Arrhenius further modified the above equation as

$$k = Ae^{-E/RT}$$

where E = activation energy for the reaction.

A = frequency factor,

R = gas constant.

Activation energy : The activation energy is the minimum energy required by a molecule to react. That is, any reaction requires the addition of energy before it can occur. This is called the activation barrier. For example, we add heat energy to bake bread or we add the enregy of friction to make a match burn. Thus, the activation energy is a threshold energy required by the reactant molecules before they can overcome an energy barrier. Only a fraction of the molecules have sufficient energy to cross the energy barrier. As the temperature increases, a greater fraction of the reactant molecules get sufficient energy to exceed the activation energy barrier. Hence, the rate of reaction increases.
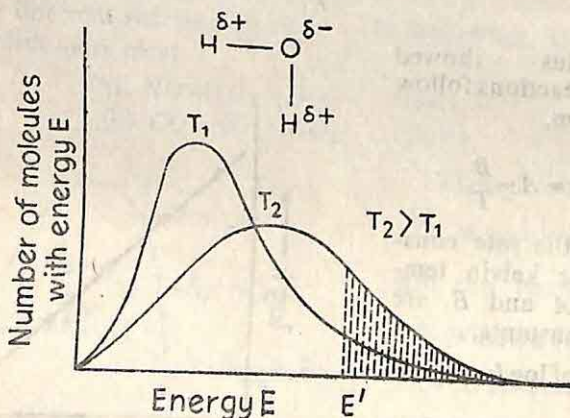
The molecular velocities of gaseous molecules are distributed according to the Maxwell's law. In such a distribution the molecules having the greatest velocities possess the greatest kinetic energies and are the molecules most likely to have enough energy to exceed the activation energy barrier. If we increase the temperature

of the gas, the distribution of molecular velocities is shifted towards higher energies, but a greater fraction of high-energy molecules enter into a reaction.

At the higher temperature T_2, a greater fraction of the molecules have energies greater than an arbitrary energy E' where E' is the activation energy barrier.

Catalyst

A catalyst is a substance that influences the rate of a chemical reaction, when used in very small amount and itself remaining unchanged at the end.

$$H_2O_2 \xrightarrow[MnO_2]{} H_2O + \tfrac{1}{2}O_2 \quad \text{(slow)}$$

$$H_2O_2 \xrightarrow[\text{Catalyst}]{} H_2O + \tfrac{1}{2}O_2 \quad \text{(rapid)}$$
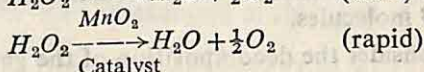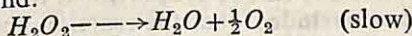
The catalyst alters the reaction rate by providing an alternative path for the reaction with a lower activation energy barrier. It is believed that the reactant molecules are absorbed on the surface of the catalyst, when they can very easily be in a position to form the activated complex.
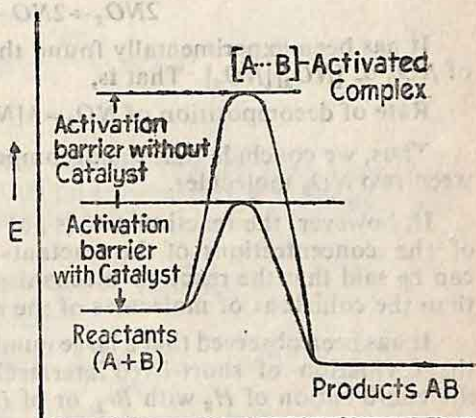
A catalyst increases both the forward reaction and the reverse reaction to the same extent so that equilibrium is established very soon. It

does not bring about any change in the equilibrium state at all. The equilibrium constant of the reaction, thus, remains unchanged.

Radiation

There are some chemical reactions which occur in the presence of light. The light radiation gives the energy needed to overcome the energy barrier and starts the reaction.

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2HCl$$
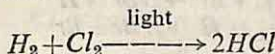
Such reactions are called **Photo-chemical Reactions**. The combination between H_2 and Cl_2 occurs in several steps.

$$Cl_2 + h\nu \text{ (light)} \rightarrow 2\overset{.}{Cl}$$
$$\overset{.}{Cl} + H_2 \rightarrow HCl + \overset{.}{H}$$
$$\overset{.}{H} + Cl_2 \rightarrow HCl + \overset{.}{Cl}$$
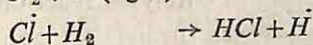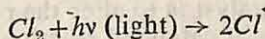
Thus, a chain reaction goes on.

Mechanism of Reaction :

The series of detailed events through which the reactants are transformed into the products is called mechanism of reaction.

The study of the rates of reaction enables us to decide whether a particular mechanism is possible or not for the reaction. For example, if it is found for a given chemical reaction involving the reactants A and B that the rate is proportional to $[A]$ multiplied by $[B]$, then it can be concluded that the reaction occurs via collision between A and B molecules.

Let us now consider the decomposition of the gas NO_2 into NO and O_2.

$$2NO_2 \rightarrow 2NO + O_2$$
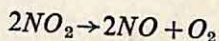
It has been experimentally found that the rate of decomposition of $NO_2 \propto [NO_2][NO_2]$. That is,

Rate of decomposition of $NO_2 = k[NO_2]^2$.

Thus, we conclude that the decomposition involves collision between two NO_2 molecules.

If, however, the reaction rate is not proportional to the product of the concentrations of the reactants as written in the equation, it can be said that the reaction mechanism involves something other than the collisions of molecules of the reactants.

It has been observed that a large number of reactions occur through the formation of short-lived **intermediates.** For example, consider the combination of H_2 with Br_2, or of H_2 with I_2.

$$H_2 + Br_2 \rightarrow 2HBr \qquad \cdots \text{(i)}$$
$$H_2 + I_2 \rightarrow 2HI \qquad \cdots \text{(ii)}$$
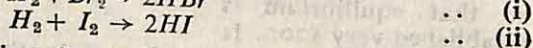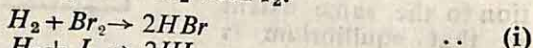
In view of these equations it may be assumed that both the reactions occur by a similar mechanism. But actually the mechanism of reaction (i) is entirely different from that of reaction (ii). It has been experimentally determined that the reaction between H_2 and Br_2 takes place via following mechanism :

$$Br_2 \rightarrow Br + Br$$
$$H_2 + Br \rightarrow HBr + H$$
$$Br_2 + H \rightarrow HBr + Br$$
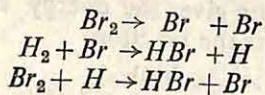
Catalytic Reaction

The function of a catalyst is to alter the rate of a reaction. There are two important types of catalysed reactions :

(i) **Homogeneous**—When the catalyst applied is in the same phase as the reactants, the catalysis is said to be homogeneous.

The reaction between SO_2 and O_2 in the gaseous medium is catalysed by NO gas in the Lead chamber process for the manufacture of SO_3.

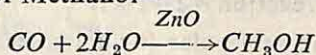$$2SO_2 + O_2 \overset{NO}{\rightleftharpoons} 2SO_3$$
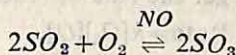
This reaction is said to be homogeneous.

(ii) **Heterogeneous**—When the catalyst used is in different phase than the reactants, the catalysis is said to be heterogeneous.

**Examples : (a)** Manufacture of Hydrogen gas from water-gas (Bosch process) provides an example of this type of catalysis.

$$CO + H_2O \xrightarrow[700\ K]{Fe_2O_3} CO_2 + H_2$$
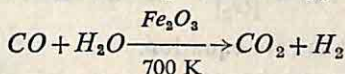
(b) Preparation of Methanol—

$$CO + 2H_2O \xrightarrow{ZnO} CH_3OH$$

Enzyme Catalysis :

Enzymes play a very important catalytic role for some very specific reactions. It is believed that an enzyme forms a complex with the molecule of a reactant (substrate). Thus,

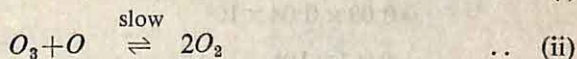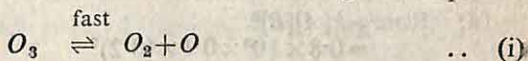$$\underset{\text{(Enzyme)}}{E} + \underset{\text{(Substrate)}}{S} \rightleftharpoons \underset{\text{(Complex)}}{ES}$$
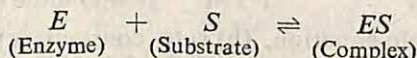
ES now breaks into the product

$$ES \rightarrow E + \underset{\text{(Product)}}{P}$$
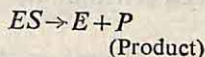
Example : (a) Urease acts as a catalyst in the hydrolysis of urea.

$$\begin{array}{c} H_2N \\ \end{array}\!\!\!\!>\!C = O + H_2O \rightarrow 2NH_3 + CO_2$$
$$\begin{array}{c} H_2N \end{array}$$

(b) Cane sugar $\xrightarrow[+H_2O]{\text{invertase}}$ Invert sugar $\xrightarrow{\text{zymase}}$ alcohol $+ CO_2$
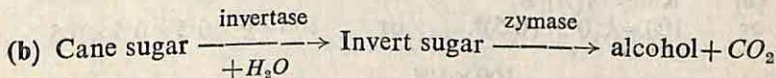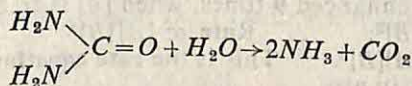
Solved Problems

1. The reaction, $2O_3 \rightleftharpoons 3O_2$ occurs in the following two steps :

$$O_3 \overset{\text{fast}}{\rightleftharpoons} O_2 + O \qquad \qquad .. \text{ (i)}$$

$$O_3 + O \overset{\text{slow}}{\rightleftharpoons} 2O_2 \qquad \qquad .. \text{ (ii)}$$

Indicate (a) the rate determining step, (ii) the rate equation, (c) order of reaction and (d) the molecularity of reaction.

(B. U. 1976)

Solution : (a) As the step (ii) is slow, it is the rate determining step.

(b) From step (ii) we get the rate of reaction.

$$\text{Rate} = k[O_3][O].$$

Now, from step (i) the equilibrium constant (K) is given by

$$K = \frac{[O_2][O]}{[O_3]}; \quad \therefore \quad [O] = \frac{K[O_3]}{[O_2]}.$$

$$\therefore \quad \text{Rate} = kK[O_3]\frac{[O_3]}{[O_2]} = K'[O_3]^2[O_2]^{-1}; \ (kK = K')$$

This is **rate equation.**

(c) $\because$ $\text{Rate} = K'[O_3]^2(O_2)^{-1},$
$\therefore$ Order of reaction $= 2 - 1 = 1.$

(d) Step (i) is mono-molecular (or unimolecular), and step (ii) is bimolecular.

2. In an experiment the following results were tabulated :

$[A]$	$[B]$	Rate
0·5 M	0·5 M	100 mole min^{-1}.
1·0 M	0·5 M	200 mole min^{-1}.
0·5 M	1·5 M	900 mole min^{-1}.

Find out, (a) rate equation, (b) rate constant, (c) order of reaction, and (d) rate of reaction, when $[A] = 0·1$, $[B] = 0·2$.

Solution : (a) It is clear from the data that rate is doubled when $[A]$ is doubled.

$$\therefore \quad \text{Rate} \propto [A].$$

Further, rate is enhanced 9 times, when $[B]$ is trebled.
i.e., $\text{Rate} \propto [B]^2$; $\therefore$ $\text{Rate} \propto [A][B]^2$
or $\text{Rate} = k[A][B]^2$. This is the **rate equation.**

(b) $\text{Rate} = k[A][B]^2$
or $100 = k(0·5)(0·5)^2$, or $100 = g \times 0·5 \times 0·5 \times 0·5$

or $$k = \frac{100 \times 10^3}{5 \times 5 \times 5} = \tfrac{4}{5} \times 10^3 = 0·8 \times 10^3.$$

(c) $\because$ $\text{Rate} = k[A][B]^2,$
$\therefore$ Order of reaction $= 1 + 2 = 3.$
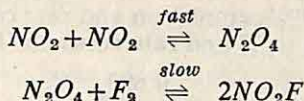
(d) $\text{Rate} = k[A][B]^2$
$$= 0·8 \times 10^3 \times 0·1 \times (0·2)^2$$
$$= 0·08 \times 0·04 \times 10^3$$

$$= \frac{8 \times 4 \times 10^3}{10^4} = 32 \times 10^{-1}$$

$$= 3·2 \text{ mole min}^{-1}.$$

3. The interaction between NO_2 and F_2 takes place according to the following mechanism :

$$NO_2 + NO_2 \overset{fast}{\rightleftharpoons} N_2O_4$$

$$N_2O_4 + F_2 \overset{slow}{\rightleftharpoons} 2NO_2F$$

Find the **rate equation** for the reaction.

Solution : The slow step is the rate determining step. Hence,
$$\text{Rate} = k[N_2O_4][F_2]$$
where k is the rate constant.

Now for the first step equilibrium constant (K) will be given by

$$K = \frac{[N_2O_4]}{[NO_2]^2} ; \qquad \therefore \quad [N_2O_4] = K[NO_2]^2$$

$$\therefore \quad \text{Rate} = kK[NO_2]^2[F_2] = K'[NO_2]^2[F_2]; \ (kK = K').$$

This is the **rate equation.**

4. The reaction, $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ is a first order reaction. The time required to decompose SO_2Cl_2 by heating to 50% of its initial amount is 60 minutes. Calculate the rate constant of the reaction at 590 K.

Solution : $\quad t_{1/2} = 60 \text{ minutes} = 60 \times 60 \text{ sec.}$

$$t_{1/2} = \frac{0 \cdot 693}{k_1} ; \ (k_1 = \text{rate constant})$$

or $\qquad k_1 = \dfrac{0 \cdot 693}{t_{1/2}} = \dfrac{0 \cdot 693}{60 \times 60} \text{sec}^{-1} = 3 \cdot 2 \times 10^{-5} \text{ sec}^{-1}.$

5. For the reaction, $2NO + O_2 \rightarrow 2NO_2$, write the equations for (a) rate of formation of NO_2, (b) rate of disappearance of NO and (c) rate of disappearance of O_2. Deduce a relation between the rate constants.

Solution : $\quad 2NO + O_2 \rightarrow 2NO_2, \qquad$ or $\qquad NO + \frac{1}{2}O_2 \rightarrow NO_2$

(a) Rate of formation of $NO_2 = \dfrac{d[NO_2]}{dt} = k_1[NO][O_2]^{\frac{1}{2}}$

(b) Rate of disappearance of $NO = -\dfrac{d[NO]}{dt} = k_2[NO][O_2]^{\frac{1}{2}}$

(c) Rate of disappearance of $O_2 = -\dfrac{d[O_2]}{dt} = k_3[NO][O_2]^{\frac{1}{2}}$

$$\frac{d[NO_2]}{dt} = -\frac{d[NO]}{dt} = -2\frac{d[O_2]}{dt}$$

$$\therefore \quad k_1[NO][O_2]^{\frac{1}{2}} = k_2[NO][O_2]^{\frac{1}{2}} = 2k_3[NO][O_2]^{\frac{1}{2}}$$
or $\qquad\qquad\qquad k_1 = k_2 = 2k_3.$

6. At 874 K the half-life period for first order thermal decomposition of acetone is 81 seconds. Calculate the time required for the reaction to go to 30% completion and rate constant.

Solution :   Half-life ($t_{1/2}$) and rate constant (k) are related as :

$$t_{1/2} = \frac{0 \cdot 693}{k}$$

or $$k = \frac{0 \cdot 693}{t_{1/2}} = \frac{0 \cdot 693}{81} \text{sec}^{-1} = 8 \cdot 55 \times 10^{-3} \text{ sec}^{-1}.$$

Now, for a first order reaction,

$$kt = 2 \cdot 303 \log \frac{a}{a-x}.$$

Here, $k = 8 \cdot 55 \times 10^{-3}$ sec^{-1}, $a = 100$ (say), $a - x = 100 - 30 = 70$.

$$\therefore \quad 8 \cdot 55 \times 10^{-3} \times t = 2 \cdot 303 \log \tfrac{100}{70}$$

or $$8 \cdot 55 \times 10^{-3} \times t = 2 \cdot 303 \times 0 \cdot 1549$$

$$\therefore \quad t = \frac{2 \cdot 303 \times 0 \cdot 1549}{8 \cdot 55 \times 10^{-3}} \text{ second} = 4 \cdot 71 \text{ s.}$$

7. An acid solution of sucrose was hydrolysed to the extent of 57% after 66 minutes. Assuming the reaction to be of first order, calculate the time taken for 75% hydrolysis.

Solution : For a first order reaction,

$$k = \frac{2 \cdot 303}{t} \log \frac{a}{a-x}.$$

$$\because \quad a = 100, \ x = 57, \ t = 67 \text{ min},$$

$$\therefore \quad k = \frac{2 \cdot 303}{66} \log \frac{100}{100-57} = \frac{2 \cdot 303}{66} \log \frac{100}{43} = \frac{2 \cdot 303}{66} \times 0 \cdot 3665$$

$$= 0 \cdot 0127.$$

Let time taken for 75% hydrolysis be t.

Then, $$k = \frac{2 \cdot 303}{t} \log \frac{100}{100-75}$$

or $$0 \cdot 0127 = \frac{2 \cdot 303}{t} \log \frac{100}{25} = \frac{2 \cdot 303}{t} \log 4$$

or $$t = \frac{2 \cdot 303}{0 \cdot 0127} \times \log 4 = \frac{2 \cdot 303}{0 \cdot 0127} \times 0 \cdot 6021 = 109 \cdot 1 \text{ min.}$$

Questions

Long Answer Type :

1. Describe in brief the factors which are responsible for influencing the rate of a reaction.

2. Explain why rise in temperature increases the rate of reaction.

3 Two gases A and B are kept in a container. What will be the effect of the following changes on the rate of reaction between these gases ?

    (i)   Pressure is doubled.

    (ii) The number of molecules of A is doubled.

    (iii) Temperature is decreased at constant volume.

4. Draw a potential energy diagram which might represent an exothermic reaction.

**5.** Distinguish between **Molecularity** and **Order of reaction**.

6. Derive an expression to relate the rate constant with the half-life of a first order reaction.

7. What do you mean by the collision theory of reaction rate ?

8. Discuss the following :

    (a) Activated complex,

    (b) Effect of catalyst on activation energy,

    (c) Rate constant.

9. Why is order of reaction and molecularity of the following reaction not the same ?

$$CH_3COOC_2H_5 + H_2O \xrightarrow{\text{H}^+} CH_3COOH + C_2H_5OH$$
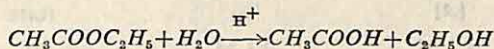
10. For the following reaction

$$A + 2B + 3C \rightarrow D + 2E$$

the rate of the reaction (R) is found to be

    (i)   proportional to the concentration of B,

    (ii) proportional to the square of the concentration of C and
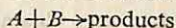
    (iii) independent of the concentration of A.

What is the order of reaction with respect to the reactants A, B and C respectively ?

What is the overall order of the reaction ?

How will you write the rate equation for the reaction ?

Is the overall order of reaction and molecularity of the reaction same or not ?

11. Determine the rate law for the reaction

$$A + B \rightarrow \text{products}$$

from the following data :

    (i)   When initial $[A]$ is doubled, initial rate doubles, and doubling the initial $[B]$, the rate is doubled.

    (ii) When the initial $[A]$ is doubled, the initial rate of reaction is doubled; doubling the initial $[B]$ cuts the rate by half.

    (iii) Doubling $[A]$, initial rate doubles, but doubling the initial $[B]$ leaves the rate unchanged.

12. Draw the energy diagram for the reaction $A + B \rightarrow AB$ in presence and absence of a catalyst. Now, answer the following :

    (i)   What is the effect of the catalyst on the energy of the reaction and the energy of the activated complex ?

    (ii) What is the effect of the catalyst on the rates of the forward and the reverse reactions ?

    (iii) What is the effect of the catalyst on the equilibrium constant ?

Short Answer Type :
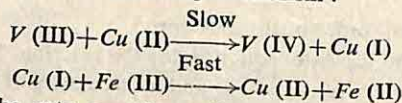
1. What is rate of reaction ?

2. What is rate constant ?

3. Explain the term 'activation energy'.

4. What do you mean by a First Order reaction ?

5. What is half-life of a reaction ?

6. In a collision of particles, what is the primary factor that determines the possibility of a reaction ?

7. How does a catalyst influence the rate constant of a reaction ?

Problems :

1. A first order reaction is said to have a rate constant $k=7.39 \times 10^{-5}$ sec^{-1}. Find the half life of the reaction.   (Ans. $t_{1/2}=9.43 \times 10^3$ sec)

2. In a certain reaction, it takes 5 minutes for the initial concentration of 0.5 mole litre^{-1} to become 0.25 mole litre^{-1} and another 5 minutes to become 0.125 mole litre^{-1}. What is the rate constant of the reaction ?   (Ans.   0.138 min^{-1})

3. Find the two-third life, $t_{2/3}$ of a first order reaction in which $k=5.48 \times 10^{-14}$ sec^{-1}.   (Ans. $t_{2/3}=2.01 \times 10^3$ sec)

4. In an experiment, the following results were obtained :

[A]	[B]	Rate
0.1 M	0.1 M	10
0.3 M	0.1 M	30
0.1 M	0.2 M	20

Find (a) rate equation, (b) order of reaction, (c) rate constant, and (d) rate when $[A]=0.2$ M and $[B]=0.5$ M.   (B. U. 1980)

5. For the reaction, $2N_2O_5 \rightarrow 4NO_2+O_2$, establish a relationship between k_1, k_2 and k_3.

6. The oxidation of Vanadium (III) by ferric ion (III) in presence of a catalyst takes place according to the following mechanism :

$$V \text{ (III)} + Cu \text{ (II)} \xrightarrow{\text{Slow}} V \text{ (IV)} + Cu \text{ (I)}$$

$$Cu \text{ (I)} + Fe \text{ (III)} \xrightarrow{\text{Fast}} Cu \text{ (II)} + Fe \text{ (II)}$$

Determine (a) the rate equation, (ii) the catalytic agent and (c) order of reaction.

7. In a reaction the following data were obtained :

[A]	[B]	[C]	Rate
0.1 M	0.1 M	0.1 M	10
0.2 M	0.1 M	0.1 M	20
0.1 M	0.3 M	0.1 M	30
0.1 M	0.1 M	0.2 M	40

Find   (a) the rate equation of the reaction,
       (b) order of reaction,
       (c) the value of the rate constant, and
       (d) rate of reaction when $[A]=0.3$ M, $[B]=0.3$ M, $[C]=0.4$ M.

                                                                    (B. U. 1974)

Objective Questions :

(A) Select True and False statements from the following :

1. The reaction between Ag^+ and Cl^- ions is instantaneous.

2. The rate of a reaction does not depend upon the concentration of the reacting species.

3. The rate of a reaction increases with rise in temperature.

4. The rate constant of a reaction is not affected by the presence of a catalyst.

5. The rate equation of a reaction is $\frac{dx}{dt} = kC_A{}^2 . C_B$. The order of reaction is 3.

(B) Below four answers to each question are given. Choose the correct answer.

1. The rate of a reaction is given by $\frac{dx}{dt} = k$ (constant). The order of the reaction is

(i) 1,   (ii) 3,   (iii) 0,   (iv) none of these.

2. The time taken for the concentration of a reactant to fall from 1 mole litre^{-1} to $0\cdot5$ mole litre^{-1} is 5 minutes.   The half-life of the reaction will be

(i) $0\cdot5$ min,   (ii) 1 min,   (iii) constant,   (iv) 5 min.

3. The rate of the reaction $A + B \rightarrow C + D$ is given by the following equation :

$$- \frac{d[A]}{dt} = k[A][B].$$

If A is present in large excess, the order of the reaction is ·
(i) 2,   (ii) 1,   (iii) 0,   (iv) $\frac{1}{2}$.

□ □ □

THERMOCHEMISTRY

Almost all chemical reactions are accompanied by energy-changes. These energy-changes apppear either in the form of evolution or absorption of heat.

The branch of chemistry which deals with the energy-changes accompanying the chemical reactions is called Thermochemistry.
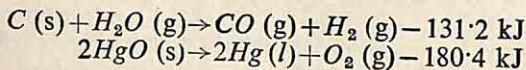
On the basis of energy-changes, the chemical reactions are of two types :

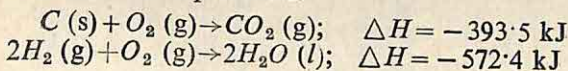(i) **Exothermic reaction**—An exothermic reaction is said to be one which is accompanied with the evolution of heat.

$$C \text{ (s)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 393.5 \text{ kJ}$$
$$2 H_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2H_2O \text{ (l)} + 572.4 \text{ kJ}$$
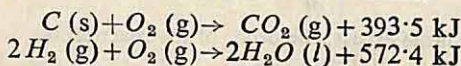
In these reactions, heat is evolved.

(ii) **Endothermic reaction**—A reaction is said to be endothermic when it is accompanied with the absorption of heat.

$$C \text{ (s)} + H_2O \text{ (g)} \rightarrow CO \text{ (g)} + H_2 \text{ (g)} - 131.2 \text{ kJ}$$
$$2HgO \text{ (s)} \rightarrow 2Hg \text{ (l)} + O_2 \text{ (g)} - 180.4 \text{ kJ}$$

In these reactions, heat is absorbed.

Thermochemical equation—The information about the evolution or absorption of heat is usually incorporated with the chemical equation for the reaction. Such an equation is known as a **Thermochemical Equation**. The heat evolved in an exothermic reaction is expressed with a negative sign to show that the reactants lose energy as they are changed into products.

$$C \text{ (s)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)}; \quad \triangle H = -393.5 \text{ kJ}$$
$$2H_2 \text{ (g)} + O_2 \text{ (g)} \rightarrow 2H_2O \text{ (l)}; \quad \triangle H = -572.4 \text{ kJ}$$

Besides, the physical states of the reactants as well as the products are also indicated in a thermochemical equation.

Similarly, heat absorbed in an endothermic reaction is expressed with a positive sign.

$$2HgO \text{ (s)} \rightarrow 2Hg \text{ (l)} + O_2 \text{ (g)}; \quad \triangle H = +180.4 \text{ kJ}.$$
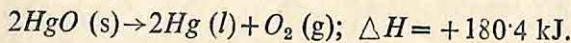
Internal or Intrinsic energy

A definite quantity of a substance possesses a fixed amount of energy associated with it under certain conditions. The energy

stored in a substance is called its **internal energy**. It is symbolised by E. The internal energy is different for different substances. Thus, the internal energy of the reactants is different from that of the products.

Suppose, the internal energy of the reactants and the products are E_R and E_P respectively. If $E_R > E_P$ then during the reaction, energy evolved $(\triangle E) = (E_R - E_P)$.

But in case, $E_R < E_P$ then in reaction, the energy absorbed $(\triangle E) = (E_P - E_R)$.

The internal energy (E) is the sum of different forms of energy such as (i) energy of translation, (ii) rotational energy of molecules, (iii) vibrational energy of molecules, (iv) coulombic energy of electrons and protons in atoms, and (v) interaction energy of the constituent particles.

The exact magnitude of internal energy cannot be determined. What is possible to determine is the change in internal energy $(\triangle E)$ when the substance passes from one state to another.

Enthalpy (H) :

A substance occupies some space according to its volume (V). It does so against the opposing influence of the atmospheric pressure (P). This makes the substance to have an additional energy (PV), due to the occupation of the space. This energy (PV) considered along with its internal energy (E) is known as the **enthalpy** (H) of the substance. Thus,

$$H = E + PV.$$

If a change occurs at a constant pressure, then

$$\triangle H = \triangle E + P \triangle V.$$

Again, $q = \triangle E + P \triangle V$

where $q =$ heat absorbed by the substance

i.e., $\triangle H = q.$

Thus, **for a change at constant pressure, the change in enthalpy is equal to the heat absorbed by the substance.**
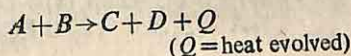
Enthalpy-changes in chemical reactions—The enthalpy-change for a chemical reaction carried out at constant pressure and temperature is expressed as

$$\triangle H = H_P - H_R$$

where $H_R =$ enthalpy of the reactants,
        $H_P =$ enthalpy of the products.

$\triangle H$ **for exothermic reaction** : Let us consider the following reaction :

$$A + B \rightarrow C + D + Q$$
$$(Q = \text{heat evolved})$$

Let H_A and H_B be the enthalpies of the reactants A and B respectively. Similarly, let the enthalpies of the products C and D be H_C and H_D respectively.

Now, the total enthalpy of the reactants $= H_A + H_B = H_R$.
The total enthalpy of the products $= H_C + H_D = H_P$.
$\therefore \quad H_R = H_P + Q$, or $\quad H_P - H_R = -Q$, or $\quad \triangle H = -Q$.
Thus, the enthalpy-change for an exothermic reaction is negative.

$\triangle H$ for an endothermic reaction :

$$A + B \rightarrow C + D - Q$$
$$H_R = H_A + H_B, \qquad H_P = H_C + H_D$$
$\therefore \quad H_R = H_P + Q$, $\qquad$ or $\quad H_P - H_R = Q$, $\qquad$ or $\qquad \triangle H = Q$
i.e., $\triangle H$ for an endothermic reaction is positive.

Enthalpy-change ($\triangle H$) is also known as the **heat of reaction**, i.e.,
$$\text{Heat of reaction} = \triangle H.$$

Heat of reaction ($\triangle H$) :

Heat of reaction is defined as the change in enthalpy when molar quantities of reactants, shown by the balanced equation for the reaction, have reacted completely.
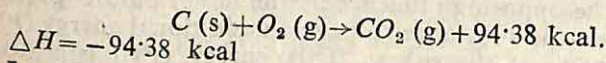
$$C \text{ (s)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 94 \cdot 38 \text{ kcal.}$$
$$\triangle H = -94 \cdot 38 \text{ kcal}$$

In this reaction, 1 mole of graphite (12 g) reacts with 1 mole of oxygen (32 g) forming 1 mole of carbon dioxide (44 g). On the completion of the reaction $94 \cdot 38$ kcal of heat is evolved.

The gaseous reactions may usually be carried out either at constant pressure or at constant volume. In such cases, the changes in enthalpy are different.

At constant pressure—When the pressure of the gaseous system is constant, the gas may expand. The expanding gas does some work. Let the volume increase from V_1 to V_2.

$\therefore$ Work done by the gas $= P(V_2 - V_1) = P \triangle V = \triangle n RT$.
$$\triangle H = \triangle E + P \triangle V, \qquad \text{or} \qquad (\triangle H)_P = \triangle E + \triangle nRT.$$
At constant volume, $\triangle V = 0$,
$\therefore \quad (\triangle H)_V = \triangle E$, $\qquad \therefore \quad (\triangle H)_P = (\triangle H)_V + \triangle n RT$.
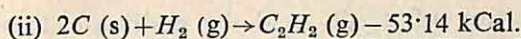$\triangle n =$ change in the number of moles of gaseous products and reactants.

Heat of Formation :

The quantity of heat evolved or absorbed when one mole of a substance is formed from its elements is called the heat of formation.
Examples : (i) $Fe \text{ (s)} + S \text{ (s)} \rightarrow FeS \text{ (s)} + 24 \cdot 0 \text{ kCal.}$
$$\therefore \quad \triangle H = -24 \cdot 0 \text{ kCal.}$$

(ii) $2C$ (s) $+H_2$ (g) $\rightarrow C_2H_2$ (g) $-53 \cdot 14$ kCal.

$\therefore$ Heat of formation of C_2H_2, $\triangle H = +53 \cdot 14$ kCal.

Standard Heat of Formation—In case the reactants and the products of the reaction are in the standard state (i.e., 298 K and 1 atmosphere), the heat-change is called the standard heat of formation.

The heat of formation of a compound is a measure of its stability. A compound having large positive heat of formation is unstable, and one having negative heat of formation is stable.

Heat of Solution :

The heat of solution is defined as the amount of heat evolved or absorbed when one mole of a solute is dissolved in a large volume of water. This can be shown as :

$$HCl \text{ (g)} + aq \rightarrow HCl aq + 75 \text{ kJ}$$
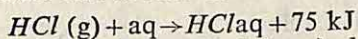
$\therefore$ Heat of solution, $\triangle H = -75$ kJ mole^{-1}.

'aq' represents a large volume of water so that further dilution causes no further heat-change.

Heat of solution may be exothermic or endothermic. Certain substance when dissolved in water may become too warm or too cold to handle comfortably.

Heat of Neutralisation :

The change in enthalpy when 1 gram-equivalent of an acid is neutralised by 1 gram-equivalent of a base in dilute solution is known as the heat of neutralisation. It may be represented as :
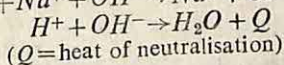
$$HCl aq + NaOH aq \rightarrow NaCl aq + H_2O + 13 \cdot 7 \text{ kCal.}$$
$$HNO_3 aq + NaOH aq \rightarrow NaNO_3 aq + H_2O + 13 \cdot 7 \text{ kCal.}$$
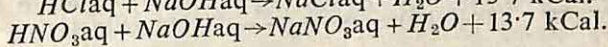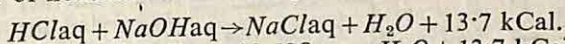
$\triangle H$ in both the cases is equal to $-13 \cdot 7$ kCal.

Heat of neutralisation involving a strong acid and a strong base is always a constant, i e., equal to $13 \cdot 7$ kCal. (Why ?)

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O + Q$$

or
$$H^+ + OH^- \rightarrow H_2O + Q$$
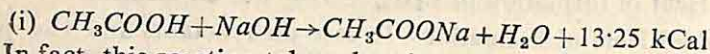$$(Q = \text{heat of neutralisation})$$
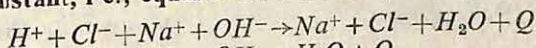
Thus, the heat of neutralisation of a strong acid and a strong base is nothing but the heat of formation of water which is $13 \cdot 7$ kCal.
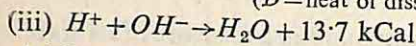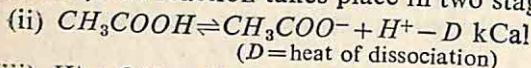
However, **the heat of neutralisation of a weak acid or a weak base is not constant**.

In such cases, in addition to neutralisation, the dissociation of the weak acid or weak base also occurs. For example, let us

consider the neutralisation of acetic acid by sodium hydroxide solution :

(i) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O + 13\cdot25$ kCal

In fact, this reaction takes place in two stages :

(ii) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+ - D$ kCal
$$(D = \text{heat of dissociation})$$

(iii) $H^+ + OH^- \rightarrow H_2O + 13\cdot7$ kCal

Adding (ii) and (iii), we get,

$$13\cdot25 = -D + 13\cdot7$$
or $$D = 13\cdot7 - 13\cdot25 = +0\cdot45 \text{ kCal.}$$

Thus, the heat of dissociation of a weak acid or base may be determined from the heat of neutralisation data.
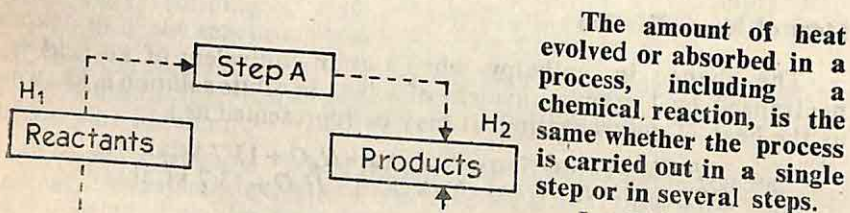
The Laws of Thermochemistry

1. Lavoisier and Laplace Law—The amount of heat required to decompose a compound into its elements is equal to the heat evolved when the same compound is formed from its elements.

i.e., Heat of dissociation $= -$ (Heat of formation)

$$CO_2 \text{ (g)} \rightarrow C \text{ (s)} + O_2 \text{ (g)}; \quad \triangle H = +393\cdot5 \text{ kJ}$$
$$C \text{ (s)} + O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} \quad ; \quad \triangle H = -393\cdot5 \text{ kJ}$$
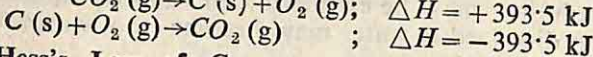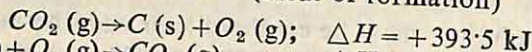
2. Hess's Law of Constant Heat Summation—This law is stated as :

(Hess's Law)

The amount of heat evolved or absorbed in a process, including a chemical reaction, is the same whether the process is carried out in a single step or in several steps.
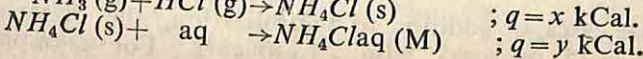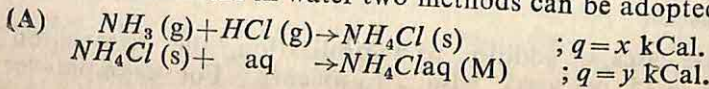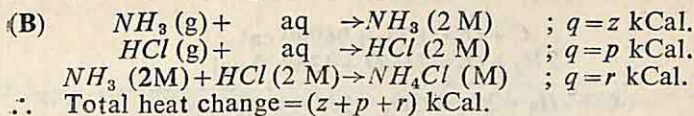
Let H_1 be the enthalpy of the reactants and H_2 that of the products. Hence, the net heat-change in the reaction, $\triangle H = (H_2 - H_1)$. The value of $\triangle H$ remains unchanged whether the reaction is carried out via step A or via step B, i.e., it is independent of the pathway between the reactants and the products.

Experimental verification—In the preparation of a molar solution of ammonium chloride in water two methods can be adopted :

(A) $NH_3 \text{ (g)} + HCl \text{ (g)} \rightarrow NH_4Cl \text{ (s)}$; $q = x$ kCal.
$NH_4Cl \text{ (s)} + \quad$ aq $\rightarrow NH_4Cl aq \text{ (M)}$; $q = y$ kCal.

∴ Total heat change $=(x+y)$ kCal.

(B) NH_3 (g) +   aq $\rightarrow NH_3$ (2 M)   ; $q=z$ kCal.
         HCl (g) +   aq $\rightarrow HCl$ (2 M)   ; $q=p$ kCal.
    NH_3 (2M) + HCl (2 M) $\rightarrow NH_4Cl$ (M)   ; $q=r$ kCal.

∴ Total heat change $=(z+p+r)$ kCal.

It is actually found that $(x+y)=(z+p+r)$.

Importance of Hess's Law—(i) With the help of Hess's law, heat changes can be evaluated for reactions which cannot be carried out in the laboratory. In such calculational methods thermochemical equations can be added, subtracted, multiplied or divided algebraically.

Bond Energy :

Bond energy for a particular type of bond in a compound is defined as the average amount of energy required to break one mole of bonds of that type present in the compound.

Bond breaking is an endothermic reaction, whereas the bond formation is an exothermic reaction.

Let us calculate the bond energy of $C-H$ bond in methane. We first determine the enthalpy change $(\triangle H)$ for the reaction

$$CH_4 \text{ (g)} \rightarrow C \text{ (g)} + 4H \text{ (g)}.$$
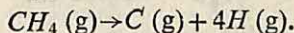
Let change in enthalpy $= \triangle H$. Then,

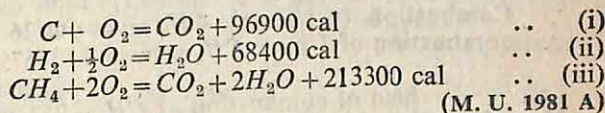$$\text{bond energy, } e_{C-H} = \frac{\triangle H}{4}$$

(as there are four $C-H$ bonds and all are equivalent). $\triangle H$ for CH_4 has been found to be 398·0 kCal. Hence,

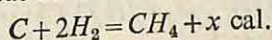$$e_{C-H} = \frac{398·0}{4} = 99·5 \text{ kCal mole}^{-1}.$$

Solved examples

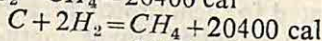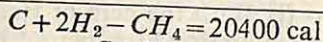1. Find the heat of formation of methane from the following data :

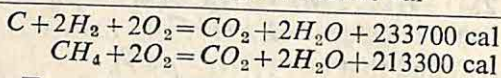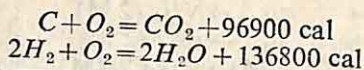$$C + O_2 = CO_2 + 96900 \text{ cal} \qquad \text{.. (i)}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68400 \text{ cal} \qquad \text{.. (ii)}$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O + 213300 \text{ cal} \qquad \text{.. (iii)}$$

(M. U. 1981 A)

Solution : Let the heat of formation of methane be x cal. Then

$$C + 2H_2 = CH_4 + x \text{ cal.}$$

Now, we have to evaluate x.

Multiply equation (ii) by 2 and then add to equation (i). From

the adduct subtract equation (iii).

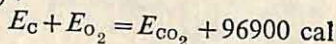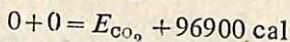$$C + O_2 = CO_2 + 96900 \text{ cal}$$
$$2H_2 + O_2 = 2H_2O + 136800 \text{ cal}$$

$$C + 2H_2 + 2O_2 = CO_2 + 2H_2O + 233700 \text{ cal}$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O + 213300 \text{ cal}$$

$$C + 2H_2 - CH_4 = 20400 \text{ cal}$$

or $\qquad C + 2H_2 = CH_4 + 20400 \text{ cal}$

i.e. $\qquad x = 20400 \text{ cal.}$

Alternatively

From equation (i) :

$$E_C + E_{O_2} = E_{CO_2} + 96900 \text{ cal}$$

or $\qquad 0 + 0 = E_{CO_2} + 96900 \text{ cal}$
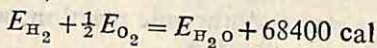
$$E_{CO_2} = -96900 \text{ cal.}$$

From equation ii) :

$$E_{H_2} + \tfrac{1}{2} E_{O_2} = E_{H_2O} + 68400 \text{ cal}$$

or $\qquad 0 + 0 = E_{HO_2} + 68400 \text{ cal}$
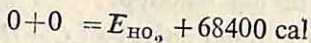
or $\qquad E_{H_2O} = -68400 \text{ cal.}$

Now, from equation (iii), we get

$$E_{CH_4} + 2E_{O_2} = E_{CO_2}\ 2E_{H_2O} + 213300 \text{ cal}$$

or $\qquad E_{CH_4} + 0 = -96900 - 2 \times 68300 + 213300$
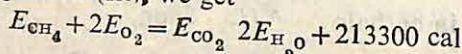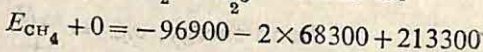
or $\qquad E_{CH_4} = -96000 - 136820 + 213300$

$$= -20400 \text{ cal.}$$

∴ Heat of formation of $CH_4 = 20400$ cal.

2. 26575 cal heat is evolved by the complete combustion of 2 g methane. Find the heat of formation of methane when the heats of formation of CO_2 and H_2O are 97000 cal and 68000 cal respectively.

(R. U. 1978 A)

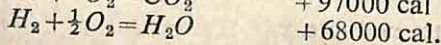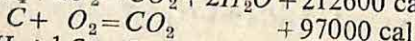**Solution :** Molecular mass of $CH_4 = 16$.

∴ 2 g $CH_4 = 2/16 = 1/8$ mole CH_4.

∵ Combustion of 1/8 mole CH_4 gives out 26575 cal of heat,

∴ combustion of 1 mole CH_4 gives out (26575×8) cal of heat

$$= 212600 \text{ cal of heat}$$

i.e., $\qquad$ heat of combustion of $CH_4 = 212600$ cal.

Now, from the data given in the question we get
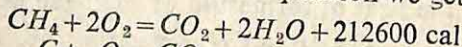
$$CH_4 + 2O_2 = CO_2 + 2H_2O + 212600 \text{ cal} \qquad .. \quad \text{(i)}$$
$$C + O_2 = CO_2 \qquad\qquad\quad + 97000 \text{ cal} \qquad .. \quad \text{(ii)}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O \qquad\qquad + 68000 \text{ cal.} \qquad .. \quad \text{(iii)}$$

We have to calculate the heat of formation of CH_4.

Let it be x cal. We should, thus, obtain the value of x in the equation—

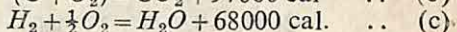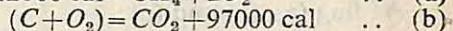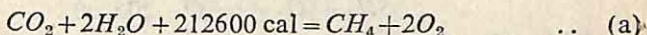$$C + 2H_2 = CH_4 + x \text{ cal.}$$

Writing equation (i) reversed, leaving other equation as they are :

$$CO_2 + 2H_2O + 212600 \text{ cal} = CH_4 + 2O_2 \qquad \text{.. (a)}$$
$$(C + O_2) = CO_2 + 97000 \text{ cal} \qquad \text{.. (b)}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68000 \text{ cal.} \qquad \text{.. (c)}$$

Multiply equation (c) by 2, and add the adduct to (a) and (b).

$$2H_2 + O_2 = 2H_2O + 136000$$
$$CO_2 + 2H_2O + 212600 = CH_4 + 2O_2$$
$$C + O_2 = CO_2 + 97000$$

$$\overline{\quad C + 2H_2 = CH_4 + 20400 \quad}$$
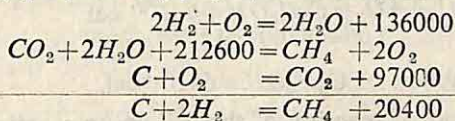
i.e., $\qquad\qquad x = 20400$ cal.

Thus, heat of formation of $CH_4 = 20400$ cal.

3. The heats of formation of $CaCO_3$, CaO and CO_2 are 288·5, 151·9 and 94·1 kCal mole^{-1} respectively. Calculate the heat of dissociation of $CaCO_3$ into CaO and CO_2. **(M. U 1973 A)**

Solution : According to the question given,

$$Ca + C + \tfrac{3}{2}O_2 = CaCO_3 + 288\cdot5 \text{ kCal} \qquad \text{.. (i)}$$
$$Ca + \tfrac{1}{2}O_2 = CaO + 151\cdot9 \text{ kCal} \qquad \text{.. (ii)}$$
$$C + O_2 = CO_2 + 94\cdot1 \text{ kCal} \qquad \text{.. (iii)}$$
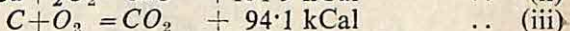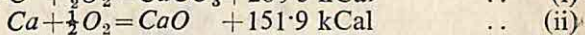
We have to determine the heat of decomposition of $CaCO_3$. As $CaCO_3$ lies on the right of equation (i), this equation is reversed sidewise, other equations being written as they are.

$$CaCO_3 + 288\cdot5 = Ca + C + \tfrac{3}{2}O_2 \qquad \text{.. (a)}$$
$$Ca + \tfrac{1}{2}O_2 = CaO + 151\cdot9 \qquad \text{.. (b)}$$
$$C + O_2 = CO_2 + 94\cdot1 \qquad \text{.. (c)}$$

Adding (a), (b) and (c) together :

$$CaCO_3 + 288\cdot5 + Ca + \tfrac{3}{2}O_2 + C = Ca + C + CaO + CO_2 + \tfrac{3}{2}O_2 + 146\cdot0$$
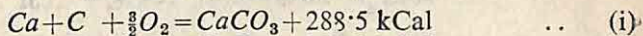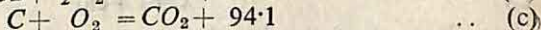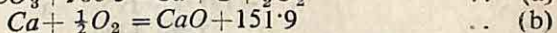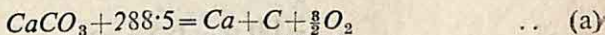$$CaCO_3 = CaO + CO_2 - 42\cdot5 \text{ kCal}$$

or,
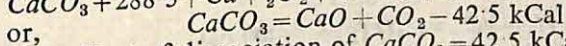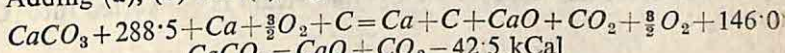
i.e., Heat of dissociation of $CaCO_3 = 42\cdot5$ kCal.

4. The heat of combustion of ethyl alcohol is 330000 cal. If the heat of formation of CO_2 and H_2O are 94300 cal and 68500 cal respectively, calculate the heat of formation of ethyl alcohol. **(Bhag. U. 1972 A)**

Solution : According to the question,

$$C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O + 330000 \text{ cal} \qquad \text{.. (i)}$$
$$C + O_2 = CO_2 + 94300 \text{ cal} \qquad \text{.. (ii)}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68500 \text{ cal.} \qquad \text{.. (iii)}$$
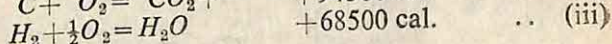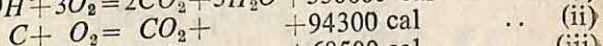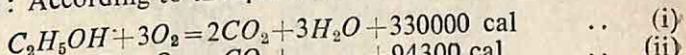
We have to find the value of x in the equation—

$$2C + 3H_2 + \tfrac{1}{2}O_2 = C_2H_5OH + x \text{ cal.}$$
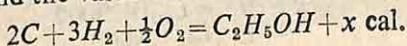
Reversing equation (i) sidewise :

$$2CO_2 + 3H_2O + 330000 = C_2H_5OH + 3O_2 \qquad \cdots \text{ (a)}$$
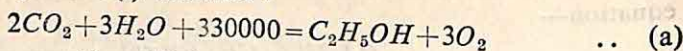
Multiplying equation (ii) by 2 and equation (iii) by 3 :

$$2C + 2O_2 = 2CO_2 + 188600 \qquad \cdots \text{ (b)}$$
$$3H_2 + \tfrac{3}{2}O_2 = 3H_2O + 205500 \qquad \cdots \text{ (c)}$$

Adding (a), (b) and (c) :

$$2CO_2 + 3H_2O + 330000 + 2C + 2O_2 + 3H_2 + \tfrac{3}{2}O_2$$

or $\qquad = C_2H_5OH + 3O_2 + 2CO_2 + 3H_2O + 394100$

i.e., $\qquad 2C + 3H_2 + \tfrac{1}{2}O_2 = C_2H_5OH + 64100 \text{ cal}$
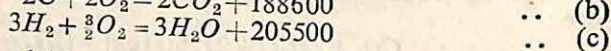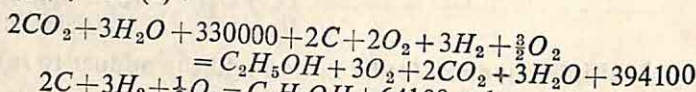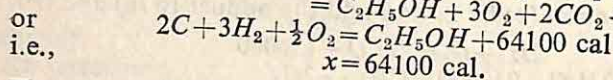
$$x = 64100 \text{ cal.}$$

Thus, heat of formation of $C_2H_5OH = 64100$ cal.

5. Calculate the heat of reaction of the following reaction :

$$CaCl_2 + 2Na = Ca + 2NaCl + x \text{ cal.}$$
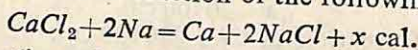
Heats of formation of $CaCl_2$ and $NaCl$ are 191 cal and 97·7 cal respectively.

Solution : By the question,

$$E_{cacl_2} + 2E_{Na} = E_{Ca} + 2E_{Nacl} + x \text{ cal} \qquad \cdots \text{ (i)}$$

$$E_{cacl_2} = -191 \text{ cal} \qquad \cdots \text{ (ii)}$$

$$E_{Nacl} = -97·7 \text{ cal} \qquad \cdots \text{ (iii)}$$

From equation (i), we get

$$E_{cacl_2} + 0 = 0 - 2 \times 97·7 + x$$

or

$$-191 = -195·4 + x$$
$$\therefore \quad x = 4·4 \text{ cal.}$$

6. From the following data, calculate the amount of heat evolved when equimolecular mixture of CO and steam is converted into CO_2 and H_2 :

$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (g)} + 58000 \text{ cal}$$
$$C + \tfrac{1}{2}O_2 = CO \quad + 29000 \text{ cal}$$
$$C + O_2 = CO_2 \quad + 96960 \text{ cal.}$$
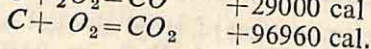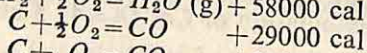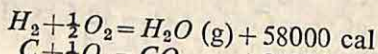
Solution :

$$E_{H_2} + \tfrac{1}{2}E_{O_2} = E_{H_2O} + 58000$$

or

$$0 + 0 = E_{H_2O} + 58000$$

or

$$E_{H_2O} = -58000 \qquad \cdots \text{ (a)}$$

Now

$$E_C + \tfrac{1}{2}E_{O2} = E_{CO} + 29000$$

or

$$0 + 0 = E_{CO} + 29000$$

or

$$E_{CO} = -29000 \qquad \cdots \text{ (b)}$$

Now $\qquad E_c + E_{O_2} = E_{CO_2} + 96960$

or $\qquad 0 + 0 = E_{CO_2} + 96960$

or $\qquad E_{CO_2} = -96960$ $\qquad$ .. (c)

$\because \quad CO + H_2O = CO_2 + H_2 + x$ cal

$\therefore \quad E_{CO} + E_{H_2O} = E_{CO_2} + E_{H_2} + x$

or $\quad -29000 - 58000 = -96960 + 0 + x$

or $\qquad x = 9960$ cal

i.e., Amount of heat evolved = 9960 cal.

7. Calculate the heat of combustion of carbon monoxide from the following data :

$$C + O_2 = CO_2 + 97000 \text{ cal} \qquad \text{.. (i)}$$
$$CO_2 + C = 2CO - 39000 \text{ cal} \qquad \text{.. (ii)}$$

(M. U. 1974 A).

Solution : In order to calculate heat of formation of carbon monoxide, we should evaluate x in equation :

$$CO + \tfrac{1}{2}O_2 = CO_2 + x \text{ cal.}$$

or $\qquad E_{CO} + \tfrac{1}{2}E_{O_2} = E_{CO_2} + x$

or $\qquad E_{CO} + 0 = E_{CO_2} + x$

or $\qquad E_{CO} = E_{CO_2} + x$ $\qquad$ .. (a)

From equation (i) :

$$E_c + E_{O_2} = E_{CO_2} + 97000$$

or $\qquad 0 + 0 = E_{CO_2} + 97000$

or $\qquad E_{CO_2} = -97000$ cal. $\qquad$ .. (b)

From equation (ii) :

$$E_{CO_2} + E_c = 2E_{CO} - 39000$$

$$E_{CO_2} + 0 = 2E_{CO} - 39000$$

or $\qquad E_{CO_2} = 2E_{CO} - 39000$

or $\qquad -97000 = 2E_{CO} - 39000$

or $\qquad 2E_{CO} = -58000$

or $\qquad E_{CO} = -29000$ cal.

or

Now, from equation (a) :

$$-29000 = -97000 + x$$
$$x = 68000 \text{ cal.}$$

or

8. The heat of combustion of C_2H_4 at 17°C and at constant volume is 332190 cal. What is the heat of combustion at constant pressure ?

Solution :
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O \ (l)$$
$$\text{1 Vol.} \quad \text{3 Vol.} \quad \text{2 Vol.} \quad 0$$

There is decrease in volume. Decrease $= 4 - 2 = 2$ vol.

$$\therefore \ (\triangle H)_P = (\triangle H)_V + \triangle n \ RT$$
$$= 332190 + 2 \times 2 \times (273 + 17)$$
$$= 333350 \text{ cal.}$$

9. The bond energies $H-H$ and $Cl-Cl$ are 430 kJ per mole and 242 kJ per mole respectively. Calculate the bond energy of HCl if the enthalpy of formation is -91 kJ per mole.
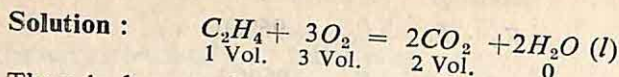
Solution : From the data, we get

$$\tfrac{1}{2}H_2 \ (g) + \tfrac{1}{2}Cl_2 \ (g) \rightarrow HCl \ (g); \quad \triangle H = -91 \text{ kJ} \qquad .. \ (a)$$
$$H_2 \rightarrow 2H \qquad ; \quad \triangle H = 430 \text{ kJ} \qquad .. \ (b)$$
$$Cl_2 \rightarrow 2Cl \qquad ; \quad \triangle H = 242 \text{ KJ} \qquad .. \ (c)$$
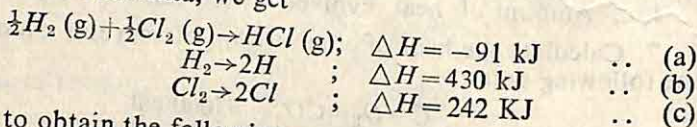
We have to obtain the following—

$$HCl \ (g) \rightarrow H \ (g) + Cl \ (g); \quad \triangle H = ?$$
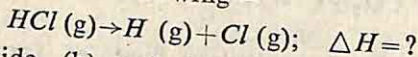
For this, divide (b) and (c) each by $\tfrac{1}{2}$ and sum up. Now, subtract the sum. from (a).

$$\tfrac{1}{2}H_2 \rightarrow H \ ; \qquad \triangle H = 215$$
$$\tfrac{1}{2}Cl_2 \rightarrow Cl; \qquad \triangle H = 121$$

Sum : $\quad \overline{\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \rightarrow H + Cl; \ \triangle H = 336}$

$$\tfrac{1}{2}H_2 \ (g) + \tfrac{1}{2}Cl_2 \ (g) \rightarrow HCl \ (g); \ \triangle H = -91$$
$$\underline{\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \quad \rightarrow H + Cl \ ; \ \triangle H = 336}$$

or $\qquad\qquad O \rightarrow -H-Cl + HCl; \quad \triangle H = -427$
or $\qquad\qquad H + Cl \rightarrow HCl \qquad\quad ; \quad \triangle H = -427$
i.e., $\qquad\qquad HCl \rightarrow H + Cl \qquad\quad ; \quad \triangle H = +427$
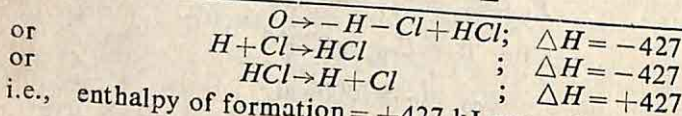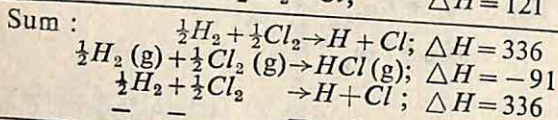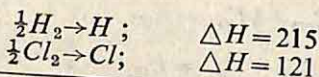
i.e., enthalpy of formation $= +427$ kJ per mole.

Questions

Long Answer Type :

1. Define the following terms :

(a) Heat of formation, (b) Heat of combustion, (c) Intrinsic energy.

2. State and explain Hess's law of constant heat summation. Illustrate its application with example.

3. Explain why the heat of neutralisation is 13·7 kCal when hydrochloric acid is neutralised with sodium hydroxide solution.

4. Explain the following terms with examples :

(a) Thermochemical equation, (b) Heat of formation, (c) Heat of combustion, (d) Heat of neutralisation, (e) Intrinsic energy.

(P. U. 1972 A; Bhag. U. 1972 A)

5. Explin 'exothermic' and 'endothermic' reactions.

6. Exaplain that $\triangle H$ for exothermic reaction is negative, while for endothermic reaction it is positive.

7. State Hess's Law and show how it is helpful in determining the heat of formation of a substance which cannot be determined directly.

8. What do you understand by internal energy and enthalpy of a substance ?

Short Answer Type :

1. What is exothermic reaction ?
2. Explain the term 'intrinsic energy'.
3. What is bond energy ?
4. Which of the following are endothermic reactions ?

(a) H_2SO_4 $(l) + H_2O$ $(l) \rightarrow H_2SO_4$ $(1 \cdot 0$ M aq); $\triangle H = -71$ kJ
(b) $C + O_2 \rightarrow CO_2$, $\triangle H = -394$ kJ
(c) $N_2 + 3H_2 \rightarrow 2NH_3$; $\triangle H = -94$ kJ
(d) $N_2 + O_2 \rightarrow 2NO$; $\triangle H = +Q$ kJ
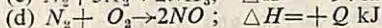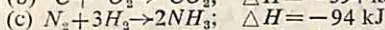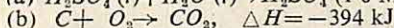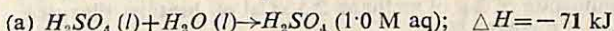
Numerical Problems :

1. Calculate the heat of formation of SO_2 from the following data :

$$PbO + \quad S \quad +3O \rightarrow PbSO_4 + 165500 \text{ cal} \quad \dots \quad \text{(i)}$$
$$PbO + H_2SO_4 \quad +\text{aq} \rightarrow PbSO_4 + H_2O + \text{aq} + 23300 \text{ cal} \quad \dots \quad \text{(ii)}$$
$$SO_2 + \quad H_2O \quad +\text{aq} \rightarrow H_2SO_4 \text{ (aq)} + 41100 \text{ cal} \quad \dots \quad \text{(iii)}$$
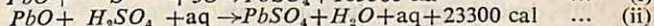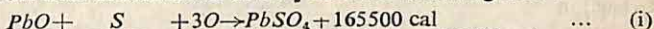
(**Ans.** 101100 cal)

2. Calculate the heat of formation of anhydrous Al_2Cl_6 from the following data :

$$2Al + 6HCl_{aq} \rightarrow Al_2Cl_{6aq} + 3H_2 + 239760 \text{ cal} \quad \dots \quad \text{(i)}$$
$$H_2 + \quad Cl_2 \quad \rightarrow 2HCl \quad +44000 \text{ cal} \quad \dots \quad \text{(ii)}$$
$$HCl + \quad \text{aq} \quad \rightarrow HCl_{aq} +17315 \text{ cal} \quad \dots \quad \text{(iii)}$$
$$Al_2Cl_6 + \quad \text{aq} \quad \rightarrow Al_2Cl_{6aq} +153690 \text{ cal} \quad \dots \quad \text{(iv)}$$
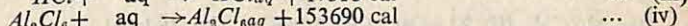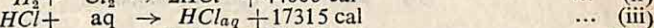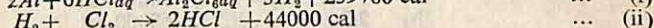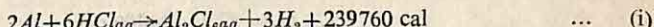
(**Ans.** 321960 cal)

3. The complete combustion of 2 g of methane evolves 26575 cal of heat. Calculate the heat of formation of methane, when the heats of formation of CO_2 and H_2O are 97000 cal and 68000 cal respectively. (**Ans.** 20400 cal)

4. For the reaction, Al_2Cl_6 (s) + $6Na$ (s) $\rightarrow 2Al$ (s) + $6NaCl$ (s), $\triangle H = -256 \cdot 0$ kCal 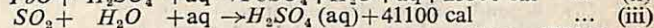at $25°C$. If the heat of formation of $NaCl$ is $-98 \cdot 3$ kCal at the same temperature, find the heat of formation of Al_2Cl_6. (**Ans.** $\triangle H = -333 \cdot 8$ kCal)

5. Find the heat of formation of benzene. Given, the heat of combustion of benzene, carbon and hydrogen to be 754300, 94380 and 6 8380 cal respectively. (**Ans.** 17120 cal)

6. The heat of combustion of CS_2 is $256 \cdot 1$ kCal. The heats of formation of CO_2 and SO_2 are $94 \cdot 3$ and $71 \cdot 0$ kCal respectively. Calculate the heat of formation of CS_2. (**Ans.** $19 \cdot 8$ kCal)

7. Calculate the heat of formation of PCl_5 (s) from the following data :

(i) $2P$ (s) + $3Cl_2$ (g) $\rightarrow 2PCl_3$ (l); $\triangle H = -151800$ cal
(ii) PCl_3 $(l) + Cl_2$ (g) $\rightarrow PCl_5$ (s); $\triangle H = -32810$ cal.
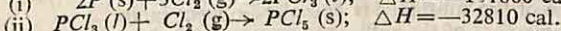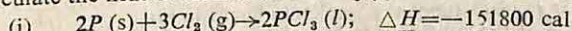
(**Ans.** 108710 cal)

Objective Questions :

1. In an exothermic reaction
   (i) heat is absorbed   (ii) heat is produced
   (iii) no heat change occurs   (iv) temperature is constant.
2. In an endothermic reaction
   (i) heat is liberated   (ii) heat is absorbed

(iii) heat is neither liberated nor absorbed
(iv) temperature changes.

3. In an exothermic reaction the reacting substances

(i) have more energy than the products
(ii) have less energy than the products
(iii) have the same energy as the products
(iv) are at higher temperature than the products.

4. Heat of combustion of a substance is always

(i) positive (ii) negative (iii) positive or negative depending on the nature of the substance (iv) an indefinite quantity.

5. In the combustion of 2 g of methane 2·5 kCal of heat is liberated. The heat of combustion of methane is

(i) 10 kCal (ii) 20 kCal (iii) 30 kCal (iv) 24 kCal.

6. The heats of combustion of benzene, carbon and hydrogen are 754300, 94380 and 68380 cals respectively. The heat of formation of benzene is

(i) 17·82 kCal (ii) 17·62 kCal (iii) 17·12 kCal (iv) 16·64 kCal.

7. According to Hess's low of constant heat summation, the heat change of a reaction

(i) depends only on the initial state
(ii) depends only on the final state
(iii) depends on both the initial and the final states
(iv) depends on none of the above.

8. The heat of formation of CO from the data

$$\text{(a)} \qquad C + O_2 \rightarrow CO_2 + 94000 \text{ cal}$$
$$\text{(b)} \qquad 2CO + O_2 \rightarrow 2CO_2 + 68000 \text{ cal}$$

is

(i) 20 kCal (ii) 22 kCal (iii) 24 kCal (iv) 26 kCal.

9. The heat of formation of Carbon disulphide is —22·06 kCals. Its intrinsic energy would be

(i) —22·06 kCal   (ii) +22·06 kCal
(iii) 11·03 kCal   (iv) —11·03 kCal.

10. The heat of formation of a compound is equal to the heat absorbed or evolved when

(i) 1 g of the compound is formed from its constituent elements
(ii) 1 mole of the compound is formed from its constituent elements
(iii) 1 g equivalent of the compound is formed from its constituent elements
(iv) 1 molecule of the compound is formed from its constituent elements.

11. The heat of combustion of a substance is the heat evolved in calories when

(i) 1 g of the substance is completely burnt in air
(ii) 1 mole of the substance is completely burnt in air
(iii) 1 g equivalent of the substance is completely burnt in air
(iv) none of the above.

12. The heat of a reaction is the heat evolved or absorbed when

(i) reactants react in the ratio of their molecular weights
(ii) reactants react in the ratio of their equivalent weights
(iii) reaction occurs in accordance with balanced chemical equation
(iv) 1 g each of the reactants react.

13. The chemical reaction which takes place with the evolution of heat is

(i) endothermic (ii) reversible (iii) oxidation (iv) exothermic.

14. The heat of neutralisation of hydrochloric acid with sodium hydroxide is

    (i) 12·5 kCal   (ii) 13·7 kCal   (iii) 1·4 kCal   (iv) 2 cal.

15. The heat of formation of H_2O is 68·3 kCal. The heat of dissociation of H_2O is

    (i) $2 \times 68·3$ kCal   (ii) 68·3 kCal   (iii) $3 \times 68·3$ kCal   (iv) $4 \times 68·3$ kCal.

16. 2·5 kcal of heat is evolved by the complete combustion of 2 g of methane. The heat of combustion of methane is

    (i) 10 kCal   (ii) 20 kCal   (iii) 30 kCal   (iv) 40 kCal.

(B) Assign mark T against the true statements and mark F against the false statements given below :

    1. The heat of reaction of an exothermic reaction is positive.

    2. The heat of reaction of an endothermic reaction is positive.

    3. The internal energy of a substance under a given set of conditions can be determined.

    4. The enthalpy of a gaseous system is expressed by the expression,

$$H = E + PV.$$

    5. (Heat of dissociation) = —(Heat of formation).

□ □ □

ELECTROCHEMISTRY

Electrolysis :

The electrolytes in aqueous solution break up into ions. When an electric current is passed through the solution of an electrolyte or through the molten electrolyte, the ions carry the current. The positively charged ions move towards the cathode and are called **cations** while the negatively charged ions move towards the anode and are called **anions**. The ions get discharged at the respective electrodes. The process is known as **electrolysis.** Thus, **the process in which a substance undergoes chemical decomposition by the passage of electricity through its aqueous solution or its molten state, is known as electrolysis.**

If the electrolyte contains only one type of cations and one type of anions then the cations are discharged at the cathode while the anions are discharged at the anode. In case, two or more types of cations or anions are present in solution then the least active ion is discharged. The decreasing order of activity of some of the ions is :

$$K \quad Na \quad Ca \quad Mg \quad Al \quad Zn \quad Fe \quad H \quad Cu \quad Hg \quad Ag$$
$$SO_4^{--} \qquad NO_3^- \quad OH^- \quad Cl^- \qquad Br^- \quad I^-$$

For example, an aqueous solution of $NaCl$ contains Na^+, Cl^-, H^+ and OH^- ions. When this solution is electrolysed, the less reactive H^+ ions are discharged at cathode instead of Na^+ ions. Cl^- ions are less reactive than OH^- ions, hence Cl^- ions are discharged at the anode.

If the electrode is active then at the cathode metal is deposited and at anode metal dissolves regardless of the activity of the other ions present in solution, e.g., Cu with $CuSO_4$, Ag with $AgNO_3$.

The relation between the amount of electricity passed and the amount of substance dissolved or deposited at the electrode is expressed by Faraday's Laws of Electrolysis.

Faraday's Laws of Electrolysis

Michael Faraday (1832), an English scientist, made two very important laws, known as Faraday's laws of electrolysis.

First Law : The mass of a substance produced or consumed at an electrode is proportional to the quantity of electricity passed through the electrolytic solution. Thus,

$$m \propto Q \qquad \text{or} \qquad m \propto ct$$

where c is the current-strength in ampere, and t is the time in second.

$$m = z.c.t$$

where z is a constant, known as the **electrochemical equivalent** of the substance.

If c and t both are equal to unity, $m = z$. This means that **the electrochemical equivalent of a substance is the mass (in grams) of the substance produced or consumed by the passage of current of 1 ampere for 1 second.**

Second Law : The second law of electrolysis may be stated as follows :

When the same quantity of electricity is passed through different electrolytes, connected in series, the amounts of different substances produced or consumed at the electrodes are directly proportional to their equivalent weights.

If the same current is passed for the same time through solutions of copper sulphate and silver nitrate, the amounts of copper and silver deposited at the cathode are proportional to their equivalent weights, i.e., $31 \cdot 78$ and $107 \cdot 8$ respectively.
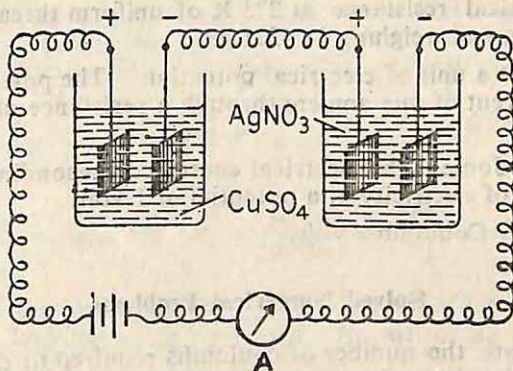
$$\frac{\text{Amount of copper deposited } (m_1)}{\text{Amount of silver deposited } (m_2)} = \frac{\text{Equivalent weight of copper}}{\text{Equivalent weight of silver}}$$

$$= \frac{E_1}{E_2}.$$

Now, according to the First law, we have

$$m_1 = z_1 c \times t \quad \text{and} \quad m_2 = z_2 c \times t$$

where z_1 and z_2 are the electrochemical equivalents of copper and silver respectively, c is the current for t second in both the solutions.

$$\therefore \quad \frac{m_1}{m_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2}.$$

Thus, the electrochemical equivalents of two substances are in the ratio of their chemical equivalents.

Electrical units :

Coulomb : The amount of electricity required to deposit by electrolysis 0·001118 g of silver from a solution containing silver ions is called a coulomb.

96,500 coulombs correspond to Avogadro's number ($6·023 \times 10^{23}$) of electron charges. This bigger unit of electricity is called a Faraday. Thus, 1 Faraday = 96,500 coulombs
$$= 6·023 \times 10^{23} \text{ electron charges.}$$

Ampere : The current-strength is measured in amperes. When one coulomb of electricity flows per second through an entire conductor, it is called one ampere.

$$\text{Coulomb} = \text{Ampere} \times \text{second.}$$

Ohm : It is a unit of resistance of a conductor. Ohm is defined as the electrical resistance at 273 K of uniform thread of mercury 106·3 cm long and weighing 14·4521 g.

Volt : It is a unit of electrical potential. The potential required to send a current of one ampere through a resistance of one ohm is called a volt.

Joule : A Joule is the electrical energy corresponding to flow of one coulomb of electricity at a potential of 1 volt.

$$\therefore \quad \text{Joule} = \text{Coulomb} \times \text{Volt.}$$

Solved Numerical Problems

1. Calculate the number of coulombs required to deposit 40·5 g of Al, when the electrode reaction is, $Al^{3+} + 3e \rightarrow Al$.

Solution : From the reaction, $Al^{3+} + 3e \rightarrow Al$, it is clear that 1 mole (27·0 g) of Al requires 3 moles of electron (3×96500 coulomb).

Thus, $\because$ 27·0 g Al requires $3 \times 96,500$ coulombs,

$$\therefore \quad 40·5 \text{ g } Al \text{ requires} \frac{3 \times 96500 \times 40·5}{27·0} \text{ coulombs}$$

$$= 4·34 \times 10^5 \text{ coulombs.}$$

2. How many gram of chlorine can be produced by the electrolysis of molten $NaCl$ with a current of 1·00 ampere for 15 minutes ?

Solution : Quantity of electricity $= c \times t = 1 \cdot 00$ amp. $\times 15 \times 60$ sec
$$= 900 \text{ coulombs.}$$

Now, $\qquad\qquad 2Cl^- \rightarrow Cl_2 + 2e$

2 moles of electrons thus produced 1 mole of chlorine, i.e.,

∵ 2×96500 coulombs produce 71 g of chlorine,

∴ 900 coulombs produce $\dfrac{71 \times 900}{2 \times 96500}$ g of chlorine $= 0 \cdot 333$ g of Cl_2.

3. Calculate the amount of silver deposited when a current of $0 \cdot 075$ ampere is passed through a solution of silver nitrate for 17 minutes.

Solution : Quantity of electricity passed
$$= 0 \cdot 075 \text{ ampere} \times 17 \times 60 \text{ sec} = 76 \cdot 50 \text{ coulomb.}$$
Equivalent weight of silver $= 108$.

Now, ∵ 96500 coulomb deposit 108 g silver,

∴ 76·50 coulomb deposit $\dfrac{108 \times 76 \cdot 50}{96500}$ gm Ag

$$= 0 \cdot 0855 \text{ gm } Ag.$$

4. An electric current is passed through the solutions of copper sulphate and silver nitrate, connected in series. If $0 \cdot 35$ gm of copper is deposited in a given time, what would be the amount of silver deposited in the same time ? $(Cu = 63 \cdot 57, \ Ag = 107 \cdot 88)$

Solution : Equivalent weight of $Cu = \dfrac{\text{At. wt,}}{\text{valency}} = \dfrac{63 \cdot 57}{2} = 31 \cdot 78.$

Equivalent weight of $Ag = \dfrac{\text{At. wt.}}{\text{valency}} = \dfrac{197 \cdot 88}{1} = 107 \cdot 88.$

$$\frac{\text{Amount of } Cu \text{ deposited}}{\text{Amount of } Ag \text{ deposited}} = \frac{\text{Eq wt. of } Cu}{\text{Eq. wt. of } Ag}.$$

∴ $\dfrac{0 \cdot 35}{x} = \dfrac{31 \cdot 78}{107 \cdot 88}$ (x = amount of Ag deposited).

∴ $x = \dfrac{0 \cdot 35 \times 107 \cdot 88}{31 \cdot 78} = 1 \cdot 18$ gm.

5. The electrochemical equivalent of silver is $0 \cdot 001118$. Find out the electrochemical equivalent of oxygen.   (Mithila U. 1976 A)

Solution : According to Faraday's second law of electrolysis,

$$\frac{\text{Electrochemical equivalent of } Ag}{\text{Electrochemical equivalent of Oxygen}}$$

$$= \frac{\text{Chemical equivalent of } Ag}{\text{Chemical equivalent of Oxygen}}$$

or $\quad \frac{z_1}{z_2} = \frac{E_1}{E_2} \quad$ or $\quad \frac{0 \cdot 001118}{z_2} = \frac{108}{8},\quad$ or $\quad z_2 = \frac{0 \cdot 001118 \times 8}{108}$

$$= 0 \cdot 0000829.$$

6. 5 gm of copper is deposited when an electric current is passed for 1930 minutes in a solution containing Cu^{++} ions. What is the strength of the current in ampere ?

What would be the amount of copper deposited when the same current is passed for the same time through a solution containing Cu^+ ions ? **(I. I. T. 1977)**

Solution : $\qquad Cu^{++} + 2e \rightarrow Cu$
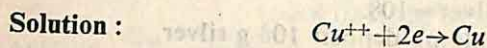
Equivalent weight of $Cu = \dfrac{\text{Atomic weight}}{2} = \dfrac{63 \cdot 5}{2} = 31 \cdot 75.$

$\qquad \because \quad 31 \cdot 75$ gm of Cu is deposited by 96500 coulomb,

$\qquad \therefore \quad 5$ gm of Cu is deposited by $\dfrac{96500 \times 5}{31 \cdot 75}$ coulomb

$$= 15,200 \text{ coulombs.}$$

Quantity of electricity in coulombs
$\qquad = \text{current-strength (ampere)} \times \text{time (sec.)}$

$\qquad \therefore \quad$ Current-strength (amp.) $= \dfrac{15200}{1930 \times 60} = 0 \cdot 131.$

In Cu^+ ions :

$$Cu^+ + e \rightarrow Cu$$
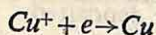
1 mole of electron deposits $63 \cdot 5$ gm Cu,
i.e., 96,500 coulombs deposit $63 \cdot 5$ gm Cu,

$\qquad \therefore \quad 15,200$ coulombs deposit $\dfrac{15200 \times 63 \cdot 5}{96500}$ gm $Cu = 10 \cdot 0$ gm Cu.

7. An electric current of $3 \cdot 7$ ampere was passed for 6 hours between nickel electrodes in $0 \cdot 5$ litre 2 M $Ni(NO_3)_2$ solution. What will be the molarity of the solution at the end of electrolysis ?
(I. I. T. 1978)

Solution : $\qquad$ Quantity of electricity $= 3 \cdot 7 \times 6 \times 60 \times 60$
$\qquad\qquad\qquad\qquad\qquad\qquad = 7 \cdot 99 \times 10^4$ coulombs.
$\qquad \therefore \quad$ 96500 coulombs liberate 1 gm equiv. Ni,

$$\therefore \quad 7 \cdot 99 \times 10^4 \text{ coulombs liberate } \frac{7 \cdot 99 \times 10^4}{96500} \text{ gm equiv. } Ni$$

$$= 0 \cdot 828 \text{ gm equiv. } Ni.$$

Valency of Ni in $Ni(NO_3)_2 = 2$.

$\qquad \therefore$ Atomic weight of $Ni = 2 \times$ Eq. wt.,

$$\therefore \quad 0 \cdot 828 \text{ Equivalent weight} = \frac{0 \cdot 828}{2} = 0 \cdot 414 \text{ mole.}$$

Initial amount of Ni in the solution $= 2 \times 0 \cdot 5 = 1 \cdot 0$ mole.

Ni liberated $= 0 \cdot 414$ mole.

$\qquad \therefore \quad Ni$ left in $0 \cdot 5$ litre solution $= 1 - 0 \cdot 414 = 0 \cdot 586$ mole.

$$\therefore \quad Ni \text{ present in 1 litre solution} = \frac{0 \cdot 586}{0 \cdot 5} = 1 \cdot 172 \text{ mole.}$$

$$\therefore \quad \text{Molarity} = 1 \cdot 172 \text{ M.}$$

8. On passing a current of $0 \cdot 5$ ampere through a solution of a salt of a metal for 32 minutes $0 \cdot 3158$ g of the metal was deposited. What is the Eq. wt. of the metal ? (Faraday $= 96,500$ coulombs)

Solution : Current $= 0 \cdot 5$ amp.

Time $= 32$ minutes $= 32 \times 60 = 1920$ sec.

$\qquad \therefore$ Quantity of electricity $= 0 \cdot 5 \times 1920 = 960$ coulombs.

$\qquad \therefore$ 960 coulombs liberate $0 \cdot 3158$ g of metal,

$$\therefore \quad 96,500 \text{ coulombs liberate} \frac{0 \cdot 3158 \times 96500}{960} \text{ g of metal} = 31 \cdot 74 \text{ g}$$

$$\therefore \quad \text{Eq. wt. of metal} = \mathbf{31 \cdot 74.}$$

9. $0 \cdot 04$ g of copper was deposited by a current of $0 \cdot 101$ ampere in 20 minutes. What are the electrochemical equivalent and equivalent weight of copper ? (Faraday $= 96,500$ coulombs)

Solution : Current $= 0 \cdot 101$ amp.

Time $= 20$ minutes $= 20 \times 60 = 1200$ sec.

$\qquad \therefore$ Quantity of electricity $= 0 \cdot 101 \times 1200 = 121 \cdot 2$ coulombs.

$\qquad \therefore$ $121 \cdot 2$ coulombs liberate $0 \cdot 04$ g of copper,

$$\therefore \quad 96,500 \text{ coulombs liberate } \frac{0 \cdot 04 \times 96500}{121 \cdot 2} \text{ g of } Cu$$

$$= 31 \cdot 85 \text{ g of } Cu.$$

i.e., Eq. wt. of copper $= 31 \cdot 85$

$$\text{Electrochemical equivalent} = \frac{31 \cdot 85}{96500} = 0 \cdot 033.$$

10. A 200 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell of negligible resistance containing a solution of Zinc chloride. What weight of Zinc will be deposited from the

solution on passing the current for 30 minutes ?
(Zn = 65·4; Faraday = 96,500 coulombs)   **(I. I. T. 1970)**

Solution: Wattage = 200,
Voltage = 110;   ∴   Ampere = $\frac{200}{110}$ = 1·82.
Time = 30 minutes = 30 × 60 = 1800 sec.
∴   Quantity of electricity = 1·82 × 1800 = 3276 coulombs.
∵   96500 coulombs liberate 32·7 g of Zinc,

∴   3276 coulombs liberate $\frac{32·7 \times 3276}{96·500}$ g of Zinc = 1·11 g of Zinc.

11. A current of 10 amperes passing for 15 minutes through a
solution of silver nitrate deposited 10·14 g of silver. Calculate the
Eq. wt. of silver. (1 faraday = 96500 coulombs)   **(Bombay F.Y. 1973)**

Solution :   Current = 10 ampere.
Time = 15 minutes = 15 × 60 = 900 sec.
∴   Quantity of electricity = 10 × 900 = 9000 coulombs.
∵   9000 coulombs liberate 10·14 g Ag,

∴   96500 coulombs liberate $\frac{10·14 \times 96500}{9000}$ g Ag = 108·72 g of Ag

i.e.,   Eq. wt. of silver = 108·72.

Applications of Electrolysis :

Some of the important applications of electrolysis are the
following :

1. In electroplating—Electroplating is the process of depositing
one metal over another with the help of electric current. This is
done to provide inert and attractive thin coatings on metals. The
metals most frequently used as plating materials are Cu, Ni, Cr, Zn
and noble metals like Ag and Au.

The metal on which electroplating is to be done is made the

Ni anode — Al spoon being nickel-Plated

Nickel ammonium sulphate solution (electrolyte)
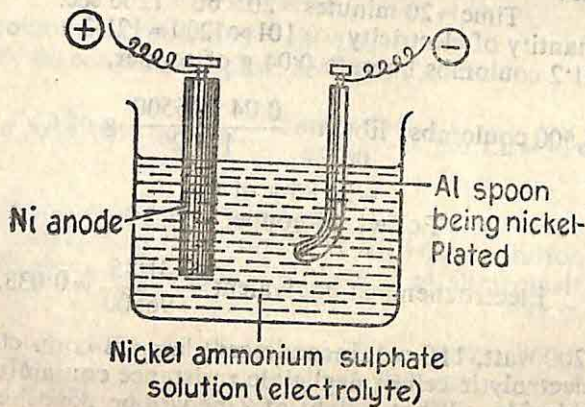
cathode (negative electrode) by connecting it to the negative pole of the battery. A water soluble salt of the metal to be deposited is used as the electrolyte.

The diagram shows the electroplating of aluminium spoon with nickel.

Reactions : The electrolyte solution contains Ni^{++}, NH_4^{+} and SO_4^{--} ions. On passing electric current the following two changes occur :

    (i) **At cathode** :

$$Ni^{++} \quad + \quad 2e \quad \rightarrow \quad Ni$$
$$\text{(from solution)} \qquad\qquad\qquad \text{(deposition on spoon)}$$

    (ii) **At anode** :

$$Ni \quad \rightarrow \quad Ni^{++} \quad + \quad 2e$$
$$\text{(from anode)} \qquad \text{(goes into solution)}$$

2. In electro-refining of metals—For this purpose, a large electro-lytic cell is set up in which impure metal sheets act as the anode and thin sheets of pure metal act as the cathode. During electrolysis impure metal dissolves at the anode, whereas metal ions from solution are deposited at the cathode as pure metal. For example, blister copper is purified by this method.

Anode : $Cu(s) \rightarrow Cu^{++}(aq) + 2e$

Cathode : $Cu^{++}(aq) + 2e \rightarrow Cu(s)$
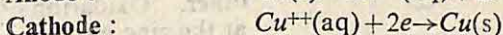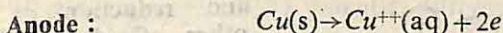
3. In electro-metallurgy—Electrolysis is employed in the isolation of a large number of metals (Na, Al, Mg, Ca, Cu etc.).
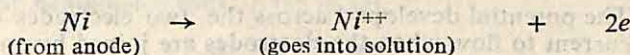
For example, in the manufacture of aluminium (by Hall's process), purified bauxite (alumina, Al_2O_3) is dissolved in molten cryolite (Na_3AlF_6) in a carbon-lined electrolytic cell. The wall of the cell acts as the cathode. A carbon anode is suspended in the electrolyte and electrolysis is carried out.

At anode : $2O^{--} + C\ (s) \rightarrow CO_2(g) + 4e$

At cathode : $Al^{+++} + 3e \rightarrow Al\ (l)$
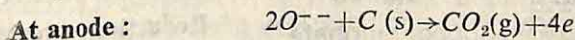
4. In the manufacture of compounds—A large number of chemical compounds are now prepared by using electrolytic methods. For example, sodium hydroxide is manufactured by the electrolysis of an aqueous solution of sodium chloride.

$$
\begin{aligned}
NaCl &\rightarrow Na^{+} + Cl^{-} &&[\times 2]\\
2Cl^{-} &\rightarrow Cl_2 + 2e &&\text{(at anode)}\\
2H_2O + 2e &\rightarrow H_2 + 2OH^{-} &&\text{(at cathode)}\\
\hline
2NaCl + 2H_2O &\rightarrow 2Na^{+} + 2OH^{-} + H_2 + Cl_2 &&
\end{aligned}
$$
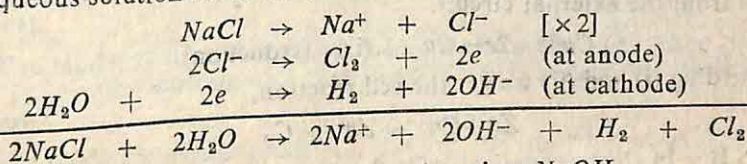
The residual solution on evaporation gives $NaOH$.

In recent years, many organic compounds have been prepared electrolytically.

Galvanic or Voltaic cell :

A galvanic cell is a device in which electrical energy is generated at the cost of oxidation-reduction reactions going on inside it.

The experimental requirements of a galvanic cell are :

(i) The oxidising and the reducing agents are kept in separate compartments called **half-cells**. Each half-cell contains a solution and a metallic conductor (i.e., electrode).

(ii) The solutions in the two half-cells are connected in some way that allows the ions to move between them.

(iii) The potential developed across the two electrodes cause an electric current to flow when the electrodes are joined by an external conducting wire.

Example—Daniel cell is a galvanic cell.

Zinc Rod

Copper vessel
Porous pot
Zinc sulphate solution
Copper sulphate solution
Copper sulphate Crystals
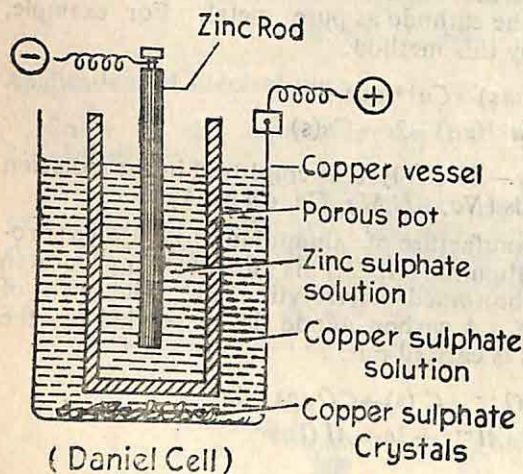
(Daniel Cell)

The working of a Daniel cell consists of oxidation at one electrode and reduction at the other. Oxidation occurs at the zinc electrode.

$$Zn \to Zn^{++} + 2e \quad ..(i)$$
(oxidation)
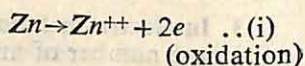
Zinc electrode is called the anode.

The electrons thus released are pushed out into the external circuit.

Reduction occurs at the copper electrode. This electrode is, therefore, called the cathode. Since there is need for electrons at the copper electrode for affecting reduction of Cu^{++} ions, the copper electrode becomes electron-deficient and it absorbs electrons from the external circuit.

$$Cu^{++} + 2e \to Cu \quad ..(ii) \quad (reduction)$$
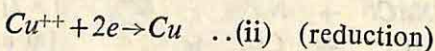
Adding (i) and (ii) we get the cell reaction,

$$Zn + Cu^{++} \to Zn^{++} + Cu$$
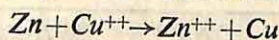
N.B.— In electrochemical cells the electrode at which oxidation

occurs is called **anode**, whereas the electrode at which reduction occurs is called **cathode**.

The Daniel's cell may be briefly represented as

$$Zn \mid Zn^{++} \parallel Cu^{++} \mid Cu$$
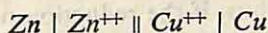
The cell is written in such a way that the negative electrode lies on the left-hand side, whereas the positive electrode is on the right-hand side.

E. M. F. of the cell :

A cell is made up of two half-cells (or electrodes). At each half-cell, there is a tendency of the metal (M) to go into solution as M^{+n} ions, leaving behind electrons on the metal.

$$M \rightarrow M^{+n} + ne$$
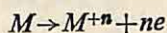
The metal thus acquires more and more negative charge. It becomes increasingly difficult for more metal ions to leave the metallic surface. A state of equilibrium is soon established. Under this condition, an electrical double layer is formed at the metal solution boundary. The metal side has excess of electrons, while the solution side has excess of M^{+n} ions. A potential difference, thuse exists at the boundary. This potential difference is called **electrode, potential**.

The two half-cells being different, the two potential differences are different. The difference of potentials between the two half-cells, when the cell is not sending current through the circuit, is known as the Electromotive Force (E. M. F.) of the cell.

Actually, E. M. F. is the maximum potential difference which the cell is capable of generating.

Potential Difference—P. D. is the difference of potentials between the two electrodes of the cell when the cell is in operation.

Single electrode potential :

Each cell is made up of two electrodes. At one electrode oxidation occurs, i.e., electrons are released, while at the other reduction takes place, i.e., electrons are taken up. Each electrode is called a half-cell.

The tendency of an electrode to lose or gain electrons when it is put in contact with its own ions in solution, is called the **electrode potential**.

The tendency to lose electrons, i.e., the tendency to get oxidised, is called **oxidation potential**.

The tendency to gain electrons, i.e., tendency to get reduced, is called **reduction potential**.

We know that reduction potential of an electrode is reverse of oxidation potential. Thus, if the reduction potential is 1·5 volt, the oxidation potential will be $-1\cdot5$ volt. Hence, both types of potentials are expressed as **oxidation potential**.

It is not possible to determine experimentally the potential of a single electrode. What is possible to determine is the difference of potentials between two electrodes by combining them to constitute a complete cell. The potential of one electrode is arbitrarily assigned a value of zero. The potentials of various other electrodes are given numerical values by comparing them with the electrode of the zero potential.

Sign of electrode potential :

(i) The potential of the electrode at which reduction occurs is given the positive sign.

(ii) The potential of the electrode at which oxidation occurs when joined to a standard hydrogen electrode is given the negative sign.

Example—Cell 1 : $Zn; Zn^{++} \mid H^+; H_2 (g), Pt$
Zinc electrode : $Zn \rightarrow Zn^{++}+2e$ (oxidation)
Hydrogen electrode : $2H^+ + 2e \rightarrow H_2 (g)$ (reduction)
Cell reaction : $\overline{Zn + 2H^+ \rightarrow Zn^{++} + H_2 (g)}$

Hence, potential of the zinc electrode is given the negative sign, i.e., $E_{Zn, Zn^{++}}$ is negative.

Cell 2 : $Pb, H_2 (g); H^+ \mid Cu^{++}; Cu$
Hydrogen electrode : $H_2 (g) \rightarrow 2H^+ + 2e$ (oxidation)
Copper electrode   : $Cu^{++} + 2e \rightarrow Cu$ (reduction)
Cell reaction   : $\overline{H_2 (g) + Cu^{++} \rightarrow 2H^+ + Cu}$
Thus, copper electrode is assigned the positive sign.

Electrochemical Series :

The potential of an electrode, at a given temperature, depends upon the concentration of the ions in solution. At 25°C, if the concentration of the ions is unity, the potential is said to be **standard electrode potential**.
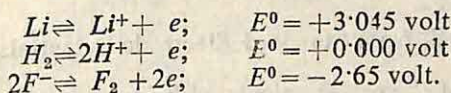
The values of standard electrode potentials, when arranged in the decreasing order, constitute the **electrochemical series**.

This series is shown in the table given below :

Electrode	Electrode reaction	E^0 (volts)
Li, Li^+	$Li \rightleftharpoons Li^+ + e$	$+3.045$
K, K^+	$K \rightleftharpoons K^+ + e$	$+2.925$
Ba, Ba^{++}	$Ba \rightleftharpoons Ba^{++} + 2e$	$+2.90$
Sr, Sr^{++}	$Sr \rightleftharpoons Sr^{++} + 2e$	$+2.89$
Ca, Ca^{++}	$Ca \rightleftharpoons Ca^{++} + 2e$	$+2.89$
Na, Na^+	$Na \rightleftharpoons Na^+ + e$	$+2.714$
Mg, Mg^{++}	$Mg \rightleftharpoons Mg^{++} + 2e$	$+2.37$
Al, Al^{+++}	$Al \rightleftharpoons Al^{+++} + 3e$	$+1.66$
Zn, Zn^{++}	$Zn \rightleftharpoons Zn^{++} + 2e$	$+0.763$
Fe, Fe^{++}	$Fe \rightleftharpoons Fe^{++} + 2e$	$+0.44$
Cd, Cd^{++}	$Cd \rightleftharpoons Cd^{++} + 2e$	$+0.403$
Co, Co^{++}	$Co \rightleftharpoons Co^{++} + 2e$	$+0.336$
Ni, Ni^{++}	$Ni \rightleftharpoons Ni^{++} + 2e$	$+0.25$
Sn, Sn^{++}	$Sn \rightleftharpoons Sn^{++} + 2e$	$+0.136$
Pb, Pb^{++}	$Pb \rightleftharpoons Pb^{++} + 2e$	$+0.126$
H_2, H^+	$H_2 \rightleftharpoons 2H^+ + 2e$	$+0.000$
Cu, Cu^{++}	$Cu \rightleftharpoons Cu^{++} + 2e$	-0.337
I^-, I_2	$2I^- \rightleftharpoons I_2 + 2e$	-0.53
Fe^{++}, Fe^{+++}	$Fe^{++} \rightleftharpoons Fe^{+++} + e$	-0.77
Hg, Hg^{++}	$Hg \rightleftharpoons Hg^{++} + 2e$	-0.789
Hg_2^{++}, Hg^{++}	$Hg_2^{++} \rightleftharpoons Hg^{++} + e$	-0.92
Ag, Ag^+	$Ag \rightleftharpoons Ag^+ + e$	-0.799
Pd, Pd^{++}	$Pd \rightleftharpoons Pd^{++} + 2e$	-0.987
Au, Au^{+++}	$Au \rightleftharpoons Au^{+++} + 3e$	-1.50
Br^-, Br_2	$2Br^- \rightleftharpoons Br_2 + 2e$	-1.065
Cl^-, Cl_2	$2Cl^- \rightleftharpoons Cl_2 + 2e$	-1.36
F^-, F_2	$2F^- \rightleftharpoons F_2 + 2e$	-2.65

Uses of Electrochemical Series :

1. The magnitude of E^0 value of an electrode is a measure of the half-cell reaction to occur in the direction shown.

$$Li \rightleftharpoons Li^+ + e; \qquad E^0 = +3.045 \text{ volt}$$
$$H_2 \rightleftharpoons 2H^+ + e; \qquad E^0 = +0.000 \text{ volt}$$
$$2F^- \rightleftharpoons F_2 + 2e; \qquad E^0 = -2.65 \text{ volt.}$$

The higher value of E^0 for $Li \rightleftharpoons Li^+ + e$, shows that Li has greater tendency to form Li^+ ion. Hydrogen has no tendency to form H^+ ions.

Similarly, negative higher value of E^0 for $2F^- \rightleftharpoons F_2 + 2e$ shows that F_2 has greater tendency to form F^- ions.

Further, Li which has the highest E^0 value is the most electropositive while F which has the least E^0 value is the most electronegative.

2. **Displacement of a metal from a solution of its salt by a metal placed above it in the electrochemical series.**

Any metal in the series can displace other metals below it from the aqueous solutions of their salts. Thus, Zn can displace Cu from $CuSO_4$ solution.

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu \downarrow$$
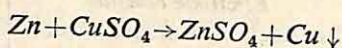
Similarly, Fe can displace Cu from $CuSO_4$ solution.

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu \downarrow$$
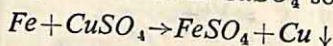
3. Prediction of reactions of Metals with acids to liberate H_2.

With the help of standard electrode potentials given in the electrochemical series, it is easy for us to predict whether a particular metal can react with acids to liberate H_2 or not.
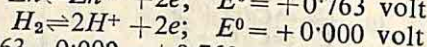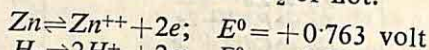
$$Zn \rightleftharpoons Zn^{++} + 2e; \quad E^0 = +0.763 \text{ volt}$$
$$H_2 \rightleftharpoons 2H^+ + 2e; \quad E^0 = +0.000 \text{ volt}$$
$$E^0 \text{ cell} = +0.763 - 0.000 = +0.763 \text{ volt} = +\text{ve}.$$

Writing of cell-reactions :

In the writing of cell reaction it should be noted that left-hand electrode of the cell is the anode (negative electrode) at which oxidation occurs, whereas the right-hand electrode is the cathode (positive electrode) at which reduction occurs.

Some examples are described below :

1. Cell : $Zn \mid Zn^{++} \parallel Cu^{++} \mid Cu$
Reaction at the anode : $Zn \rightarrow Zn^{++} + 2e$
Reaction at the cathode : $Cu^{++} + 2e \rightarrow Cu$
$\therefore$ **Cell reaction :** $Zn + Cu^{++} \rightarrow Zn^{++} + Cu.$

2. $Zn \mid ZnCl_2 \parallel H^+ \mid H_2, \; Pt$
Anode reaction   : $Zn \rightarrow Zn^{++} + 2e$
Cathode reaction   : $2H^+ + 2e \rightarrow H_2$
$\therefore$ **Cell reaction** : $Zn + 2H^+ \rightarrow Zn^{++} + H_2$
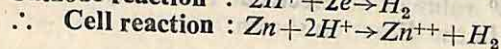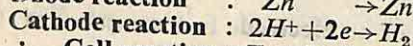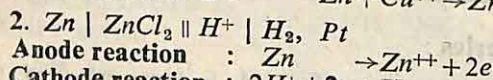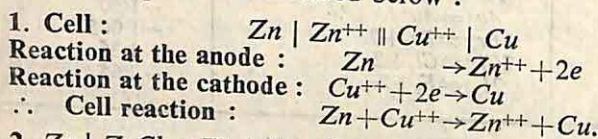
E. M. F. of the Cell from Standard Electrode Potentials :

The e. m. f. of the cell is calculated by subtracting the reduction potential of the left-hand electrode from that of the right-hand electrode. Thus,

$$E_{cell} = E_{right} - E_{left} = E_{cathode} - E_{anode}$$

Example 1.—Calculate the e. m. f. of the following cells :

(i) $Zn \mid Zn^{++} \; (1.0 \text{ M}) \parallel Cu^{++} \; (1.0 \text{ M}) \mid Cu$
(ii) $Ag \mid Ag^+ \; (1.0 \text{ M}) \parallel Cu^{++} \; (1.0 \text{ M}) \mid Cu$
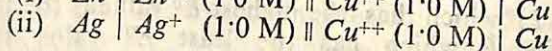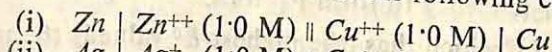
Solution : (i) $E^0_{zn/zn^{++}} = +0.763$ volt, and $E^0_{cu/cu^{++}} = 0.337$ volt.
$\therefore$ $E^0_{zn^{++}/zn} = -0.763$ volt, $E^0_{cn^{++}/cu} = +0.337$ volt
$\therefore$ $E_{cell} = +0.337 - (-0.763) = +1.100 = +1.10$ volt.

(ii) $E^0_{Ag/Ag^+} = -0.799$ volt; $E^0_{Cu/Cu^{++}} = -0.337$ volt
$\therefore \quad E^0_{Ag^+/Ag} = +0.799$ volt; $E^0_{Cu^{++}/Cu} = +0.337$ volt
$\therefore \quad E_{cell} = +0.337 - (+0.799) = +0.337 - 0.799 = -0.462$ volt.

Example 2. On the basis of data given below, predict whether zinc would be oxidised or not when placed in contact with a solution of nickel sulphate.

$$Ni^{++} + 2e \rightarrow Ni, \quad E^0 = -0.25 \text{ volt}$$
$$Zn^{++} + 2e \rightarrow Zn, \quad E^0 = -0.76 \text{ volt.}$$

Solution :

$$Zn \rightarrow Zn^{++} + 2e, \quad E_{oxtd.} = +0.76 \text{ volt}$$
$$Ni^{++} + 2e \rightarrow Ni, \quad E_{red.} = -0.25 \text{ volt}$$

$$\therefore \quad Zn + Ni^{++} \rightarrow Zn^{++} + Ni$$

and $\qquad E_{cell} = 0.76 - 0.25 = 0.51$ volt
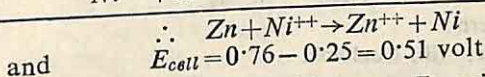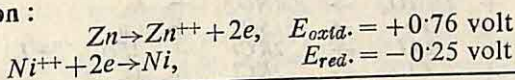
As the e. m. f. of the cell is $+$ve, Zn will be oxidised to Zn^{++}.

Questions

Long Answer Type :

1. What are Faraday's Laws of Electrolysis ? How would you verify the laws ? (M. U. 1973 A)

2. State Faraday's Laws of Electrolysis. Show that the electrochemical equivalents of elements are proportional to their chemical equivalents.

3. What do you understand by electrolysis ? How would you study the electrolysis of molten sodium chloride ?

4. What is a galvanic cell ? What is the source of electrical energy in a galvanic cell ?

5. Explain clearly what you understand by 'single electrode potential'. Is it possible to measure a single electrode potential ?

6. What is meant by electrochemical series ? Describe briefly the various uses of this series.

7. The values of some standard electrode potentials are :

$$
\begin{array}{llllll}
Cu^+ & \rightarrow & Cu^{++} & + & e, & E^0 = -1.5 \text{ volt} \\
Fe^{++} & \rightarrow & Fe^{+++} & + & e, & E^0 = -0.77 \text{ volt} \\
Hg^+ & \rightarrow & Hg^{++} & + & e, & E^0 = -0.92 \text{ volt} \\
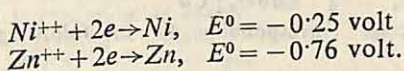2Br^- & \rightarrow & Br_2 & + & 2e, & E^0 = -1.07 \text{ volt.}
\end{array}
$$
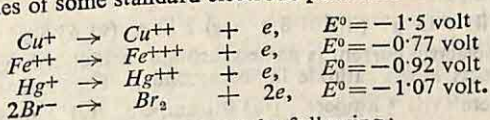
On the basis of these values, answer the following :

(i) Can Fe^{++} ion reduce the Cu^{++} ion ?

(ii) What will be the reaction if a solution containing Fe^{++} ions is mixed up with a solution containing Hg^{++} ions ?

(iii) Which of the following is the best reducing agent ? $Cu^+, Fe^{++}, Hg^+, Br^-$.

8. Describe any two uses of electrolysis.

Short Answer Type :

1. What is electrolysis ?
2. State the two laws of electrolysis.
3. Describe the functioning of a Daniel's cell.

4. What is an electrode ?

5. What do you mean by a cell reaction ?   Give your answer with reference to the Daniel's cell.

6. Write down the cell reactions in the following cells :

   (i) $Pt, H_2 \mid H^+$ $\parallel$ $Fe^{+++}, F^{++} \mid Pt$
   (ii) $Zn \mid Zn(NO_3)_2$ $\parallel$ $AgNO_3 \mid Ag$
   (iii) $Cd \mid Cd^{++}$ $\parallel$ $Cu^{++} \mid Cu$
   (iv) $Zn \mid ZnSO_4$ $\parallel$ $CaSO_4 \mid Cd$ **(B. U. 1976)**

7. Represent cells corresponding to the following oxidation-reduction reactions :

   (i) Zn $+$ $2HNO_3$ $\rightarrow$ $Zn(NO_3)_2$ $+$ H_2
   (ii) $CuSO_4$ $+$ Fe $\rightarrow$ $FeSO_4$ $+$ Cu
   (iii) $2FeCl_3$ $+$ $2KI$ $\rightarrow$ $2KCl$ $+$ $2FeCl_2$ $+ I_2$
   (iv) $2KI$ $+$ Cl_2 $\rightarrow$ $2KCl$ $+$ I_2

8. Explain the following terms :

   (i) Anode, (ii) Cathode, (iii) Coulomb.

9. What is a half-cell ?

10. In the light of electrochemical series, say whether the following reactions would occur or not :

   (i) Silver is allowed to react with Oxygen.
   (ii) Tin is placed in a hydrochloric acid solution.
   (iii) Zinc is heated in steam.
   (iv) SnO_2 is heated in a current of H_2.

11. What is electroplating ?

Objective Questions :

(A) 1. When 96500 coulombs of electricity is passed through a dilute solution of sulphuric acid, the volume of hydrogen liberated at N.T.P. is

   (i) 5·6 litres (ii) 11·2 litres (iii) 22·4 litres (iv) 1 litre.

2. 96500 coulombs of electricity liberates from a solution of $CuSO_4$

   (i) 73·5 g of Cu (ii) 31·76 g of Cu
   (iii) 96500 g of Cu (iv) 100 g of Cu.

3. The weight of Cu deposited by 0·2 Faraday of electricity passed through a solution of $CuSO_4$ is

   (i) 6·35 g (ii) 3·18 g (iii) 31·8 g (iv) 2·12 g (v) 63·5 g. **(P.M.D.T. 1973)**

4. When an electric current is passed through acidulated water, 112 ml of H_2 at N.T.P. collects at the cathode in 965 seconds. The current strength is

   (i) 1 ampere (ii) $\frac{1}{2}$ ampere (iii) 0·1 ampere (iv) 2 ampere.

5. What will be the weight of silver deposited from silver nitrate solution by 0·5 Faraday of electricity ? (at. wt. of $Ag=108$)

   (i) 5·4 g (ii) 10·8 g (iii) 21·6 g (iv) 54 g (v) 108 g. **(P.M.D.T. 1976)**

6. An electrolyte

   (i) gives H^+ ions in aqueous solution
   (ii) has ions even in the solid state
   (iii) is highly soluble in water
   (iv) does not ionise in solution.

7. Which of the following is an electrolyte ?

   (i) urea (ii) glucose (iii) sodium nitrate (iv) canesugar.

8. In electrolysis the process which occurs at the cathode is

   (i) oxidation (ii) decomposition (iii) reduction (iv) association.

9. During electrolysis the reaction which takes place at the anode is

(i) ionisation   (ii) oxidation   (iii) reduction   (iv) dissociation.

10. The substance which conducts electricity with decomposition is called

(i) conductor   (ii) insulator   (iii) electrolyte   (iv) non-electrolyte.

11. In the electrolysis of dil. H_2SO_4 using platinum electrodes

(i) OH^- ion is discharged at the cathode
(ii) hydrogen is evolved at the anode
(iii) oxygen is the only gas evolved
(iv) sulphur is deposited at the cathode.

12. During electrolysis of $NaOH$ solution in water

(i) Na is liberated at the cathode and O_2 at the anode
(ii) H_2 is liberated at the cathode and O_2 at the anode
(iii) Na is deposited at the anode
(iv) None of the above.

13. What will be the value of current strength if it deposits $1·5$ gm of silver in 30 minutes ?   (E.C.E. of silver is $0·0001118$ g/coulomb)

(i) $0·747$ A   (ii) $0·846$ A   (iii) $0·647$ A   (iv) $0·477$ A.

14. Which of the following will not conduct electricity ?

(i) Na^+Cl^- (aqueous solution)   (ii) Na^+Cl^- (solid)
(iii) Na^+Cl^- (fused)   (iv) graphite.

15. How long would it take a current of 3 amperes to decompose 18 g of water ?   (Equivalent weight of hydrogen $=1$ and that of oxygen $=8$)

(i) 8 hours   (ii) 18 hours   (iii) 2 hours   (iv) 6 hours.

16. A current of $1·5$ amperes is passed in copper voltameter for 20 minutes and the weight of copper deposited is $1·591$ g.   Calculate E.C.E. of copper.

(i) $3·2 \times 10^{-4}$ gm/coulomb   (ii) $2·2 \times 10^{-4}$ gm/coulomb
(iii) $1·2 \times 10^{-4}$ gm/coulomb   (iv) $4·2 \times 10^{-4}$ gm/coulomb.

17. One Faraday of electricity liberates from a solution of silver nitrate

(i) 2 gm-equiv. silver   (ii) 108 g of silver
(iii) 54 g of silver   (iv) 1 gm atom of silver.

18. The electrode potentials of the five elements A, B, C, D and E are $-1·36$, $-0·32, 0, -1·26$ and $-0·42$.   The order of reactivity of these elements will be

(i) A, D, E, B and C (ii) C, B, E, D and A (iii) B, D, E, A and C.

19. In the electrochemical series the elements are arranged on the basis of

(i) electrode potentials   (ii) electrical conductivity
(iii) chemical affinity   (iv) oxidation number.

20. 965 coulombs of electric current was passed through $NaOH$ solution. The volume of oxygen liberated at N.T.P. at anode is

(i) 56 ml   (ii) 112 ml   (iii) 224 ml   (iv) 448 ml.

21. When an electric current is passed through acidulated water, 112 ml of H_2 gas at N.T.P. collects at the cathode in 965 sec.   The current strength is :

(i) 1 amp.   (ii) $\frac{1}{2}$ amp.   (iii) $0·1$ amp.   (iv) 2 amp.

22. A conducting solution—

(a) must contain electrons (ii) can be made by dissolving sodium chloride in water (iii) can be made by dissolving hydrogen chloride in water (iv) must have ions (v) can be made by dissolving carbon tetrachloride in water.

(B) State whether the following statements are true or false :

1. In the electrolysis of molten potassium chloride, chlorine is liberated at the cathode.   (I.I.T. 1978)

2. A small amount of acid or alkali is added before the electrolysis of water.

3. In a galvanic cell, electrical energy is produced at the cost of chemical reactions.

4. The maximum weight of silver which can be displaced from $AgNO_3$ solution by 0·1 gm equivalent of Mg is 2·2 g.

Numericals :

Based on Faraday's Laws—

1. 0·1918 g of Cu is deposited when an electric current of 0·1 ampere is passed for 100 minutes through $CuSO_4$ solution. Find the electrochemical equivalent of Cu.   (B. U. 1973)

2. Silver is electro-deposited on a metallic vessel of surface area 800 cm² by passing a current of 0·20 ampere for 3·0 hours. Calculate the thickness of silver deposited, given its density as 10·47 g/ml.   (I. I. T. 1978)

[Ans. Current=0·2 amp., Time=3 hours.

$\therefore$ Quantity of electricity$=\dfrac{0·2\times 3\times 60\times 60}{96500}$ Faraday

$\therefore$ Weight of silver deposited$=\dfrac{0·2\times 3\times 60\times 60}{96500}\times 107·92=2·42$ g.

(Equiv. wt. of $Ag=107·92$)

Let the thickness of silver deposited be x cm.

$\therefore$ Volume of Ag deposited $=$ area $\times$ thickness
$$=(800\times x)\text{ cm}^3.$$

$\because$ Weight$=$Volume$\times$density,

$\therefore$ 2·42 g$=(800\times x)$ cm³ $\times 10·47$ g/cm³

or $x=\dfrac{2·42}{800\times 10·47}=0·000288.$

$\therefore$ Thickness of $Ag=2·88\times 10^{-4}$ cm.]

3. Calculate the amount of Cu deposited when a current of 5 amperes is passed through a copper sulphate solution for 30 minutes. ($F=96,500$ coulombs).

(Ans. 1·48 g)

4. An electric current is passed through solutions of $CuSO_4$ and $AgNO_3$, connected in series. If 1·68 g of Ag is deposited in a given time, how much Cu would be deposited in the same time ? ($Cu=63·57$; $Ag=107·88$). (R. U. 1976 A)

(Ans. 0·494 g)

5. How much time would be required for a current of 0·15 amp. to liberate 20 mg Cu from a $CuSO_4$ solution ? ($Cu=64$, $F=96,500$ coulombs)

(P. U. 1976 A)

6. An electric current is passed through molten magnesium compound for 40 minutes, when 0·01 g atom of magnesium is deposited at the cathode. How much time will be needed to liberate 0·01 g atom of aluminium by passing the same current through a molten aluminium compound ?   (I. S. C. Delhi 1979)

7. An electric current equivalent to that present on 1 mole of electrons is passed separately through $CuSO_4$ and H_2SO_4 solutions. Find out

(i) What are masses of liberated copper and hydrogen ?

(ii) What is the value of Avogadro's number, when 0·16 g of *Cu* is liberated on passing a current of 0·5 amp. for 16 minutes ?   (I. S. C. Delhi 1977)

8. The same quantity of electricity passed through suitable voltameters in series, liberates 1·12 litres of hydrogen at N. T. P. and deposits 0·90 g of a metal. Calculate the Eq. wt. of the metal.
                                                                            (Ans. 9)

9. How many hours are required for a current of 3·0 amperes to decompose electrolytically 18 g of water ?
                                                                          (Ans. 18 hr)

10. An electrolytic cell contains a solution of $CuSO_4$ and an anode of impure copper. How much copper will be refined (i.e., deposited on the cathode) by 150 amperes maintained for 12 hours ?   (Ans. 2·1 kg *Cu*)

□ □ □

COLLIGATIVE PROPERTIES OF SOLUTIONS

A **colligative property** is that property which depends upon the number of solute particles present in the solution. It does not depend upon the chemical nature of solute particles. In solution the solute particles should not undergo association or dissociation. In case of association, the number of particles actually added becomes small and hence the value of the colligative property is lowered. In case of dissociation, the number of solute particles actually added becomes larger and hence the colligative property is increased.

Some of the colligative properties of a solution are—

(i) Lowering of vapour pressure,
(ii) Osmotic pressure,
(iii) Elevation of boiling point, and
(iv) Depression of freezing point.

Lowering of Vapour Pressure

When a non-volatile solute is dissolvd in a liquid solvent, the vapour pressure of the solvent is lowered.

Thus, if P_0 is the vapour pressure of a pure solvent and P_s that of the solution, then, $(P_0 - P_s)$ is called **lowering of vapour pressure.**

Relative Lowering of Vapour Pressure—The lowering of vapour pressure $(P_0 - P_s)$ when divided by the vapour pressure of the pure solvent (P_0) is called **relative lowering of vapour pressure,** i.e.,

$$\text{Relative Lowering of Vapour Pressure} = \frac{P_0 - P_s}{P_0}.$$

According to Raoult's law, $P_s = P_0 \times n$, where $n =$ mole fraction of the solute. Since n is a positive quantity and is smaller than unity, P_s is always less than P_0.

Molecular Weight of Solute from lowering of Vapour Pressure :

Let w gm of a solute of molecular weight m be dissolved in W gm of solvent of molecular weight M.

∴ Number of moles of solute $= w/m$
Number of moles of solvent $= W/M$
Total number of moles in solution $= (w/m + W/M)$.

$$\therefore \quad \text{Mole fraction of solute} = \frac{w/m}{(w/m + W/M)} = n.$$

Since w is very small hence $(w/m + W/M)$ is approximately equal to W/M.

$$\therefore \quad n = \frac{w/m}{W/M} = \frac{w.M}{W.m}.$$

Now, according to Raoult's law,

$$\frac{P_0 - P_s}{P_0} = \frac{w.M}{W.m}, \quad \text{or} \quad m = \frac{w.M}{W\left(\dfrac{P_0 - P_s}{P_0}\right)}.$$

Determination of the Lowering of Vapour Pressure :

Ostwald and Walker's method—In this method, a current of the same volume of dry gas (air) is passed through (i) the solution, (ii) the solvent and (iii) a suitable absorber to absorb the vapour of the solvent. Anhydrous $CaCl_2$ is found to be a good absorber.

The following arrangement of apparatus is used to determine the relative lowering of vapour pressure :
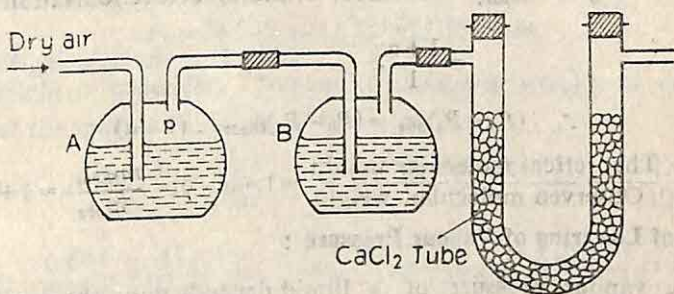
A current of dry air is slowly passed through the sets of bulbs A and B. The solution is placed in A and pure solvent in B. These two sets of bulbs are followed by $CaCl_2$ tubes. The bulbs are placed in a constant temperature bath (thermostat). The air passing through the solution gets saturated with the solvent vapour from the solution. The quantity of solvent vapour carried by the air from bulbs A is proportional to the vapour pressure of solution (P_s). When the air passes through the bulbs B, it takes more solvent vapour from the bulbs B and becomes saturated at the pressure of the pure solvent (P_0) which is higher than P_s. The quantity of solvent vapour taken from the bulbs B is proportional to $(P_0 - P_s)$. The total quantity of solvent vapour taken out from both A and B is proportional to P_0.

Thus, the bulbs A and B are weighed before and after the experiment. The $CaCl_2$ tube is also weighed before and after the experiment.
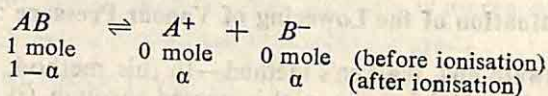
Difference in weights of $B \propto (P_0 - P_s)$.

Difference in weights of $CaCl_2$ tube $\propto P_0$.

$$\therefore \quad \frac{\text{Loss in weight of solvent}}{\text{Gain in weight of } CaCl_2 \text{ tube}} = \frac{P_0 - P_s}{P_0}.$$

Abnormal lowering of vapour pressure : If a solute ionises in solution, the observed lowering of vapour pressure is found to be greater than the theoretically possible value. This is because the number of particles in solution increases due to ionisation of the solute. $NaCl$, $NaNO_3$, $BaCl_2$, KCl etc. show such a behaviour.

Suppose a molecule AB ionises in solution according to the following equation :

$$
\begin{array}{ccccc}
AB & \rightleftharpoons & A^+ & + & B^- \\
1 \text{ mole} & & 0 \text{ mole} & & 0 \text{ mole} \quad \text{(before ionisation)} \\
1-\alpha & & \alpha & & \alpha \quad \text{(after ionisation)}
\end{array}
$$

α is the degree of ionisation.

Number of molecules after ionisation
$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha,$$

$$\therefore \quad \frac{(P_0 - P_s)_{obs.}}{(P_0 - P_s)_{theor.}} = \frac{\text{Number of moles after ionisation}}{\text{Number of moles before ionisation}}$$

$$= \frac{1+\alpha}{1}.$$

$$\therefore \quad (P_0 - P_s)_{obs.} = (P_0 - P_s)_{theor.} \cdot (1+\alpha)$$

or $\quad \dfrac{\text{Theoretical molecular weight}}{\text{Observed molecular weight}} = 1 + \alpha \quad$ or $\quad \dfrac{m_{theor.}}{m_{obs.}} = 1 + \alpha.$

Cause of Lowering of Vapour Pressure :

The vapour pressure of a liquid depends upon the number of liquid molecules per unit volume which escape into the vapour phase. Again, the number of escaping molecules depends upon the total number of molecules per unit volume of the liquid. When a solute is dissolved in the liquid, the number of molecules of the liquid in an unit volume of it decreases. Hence, the number of the molecules escaping into the vapour phase decreases. The vapour pressure of the liquid is thus lowered.

Derivation of Raoult's Law :

Let n moles of a solute be dissolved in N moles of a solvent. The vapour pressure of the solvent above the solution is proportional

to the mole fraction of the solvent in the solution, i.e.,

$$P_s \propto \frac{N}{n+N}$$

or $\quad P_s = K \dfrac{N}{n+N}$, where K is a constant.

In a pure solvent, $n = 0$ and $P_s = P_0$.

$\therefore \quad P_0 = K.$ $\qquad \therefore \quad P_s = P_0 \cdot \dfrac{N}{n+N}$ $\quad$ or $\quad \dfrac{P_s}{P_0} = \dfrac{N}{n+N}$

or $\quad 1 - \dfrac{P_s}{P_0} = 1 - \dfrac{N}{n+N}$ $\quad$ or $\quad \dfrac{P_0 - P_s}{P_0} = \dfrac{n}{n+N}.$

Thus, the relative lowering of vapour pressure is equal to the mole fraction of the solute. This is Raoult's Law.

Solved Problems

1. The vapour pressure of a solution containing 13 gm of solute in 1000 gm of water at 28°C is 27·371 mm. Calculate the molecular weight of the solute. The vapour pressure of water at this temperature is 28·065 mm.

Solution : By the question,

$$P_0 = 28\cdot065 \text{ mm}, \quad P_s = 27\cdot371 \text{ mm}.$$

Weight of solute $(w) = 13$ gm.
Weight of water $(W) = 100$ gm; its molecular weight, $M = 18$.

Let the molecular weight of the solute be m.

Now $\quad \dfrac{P_0 - P_s}{P_0} = \dfrac{wM}{W.m}$ $\quad$ or $\quad \dfrac{28\cdot065 - 27\cdot371}{28\cdot065} = \dfrac{13 \times 18}{100 \times m}$

or $\quad \dfrac{0\cdot694}{28\cdot065} = \dfrac{13 \times 18}{100 \times m}$ $\quad$ or $\quad m = \dfrac{13 \times 18 \times 28\cdot065}{0\cdot694 \times 100} = 94\cdot6.$

2. The vapour pressure of water at 20°C is 17·0 mm. Calculate the vapour pressure of a solution of 3 gm of urea in 50 gm of water. Molecular weight of water is 18 and that of urea is 60.

Solution. By the question, we have

$$P_0 = 17\cdot0 \text{ mm}, \quad P_s = ?$$
$$w = 3 \text{ gm}, \quad m = 60,$$
$$W = 50 \text{ gm}, \quad M = 18.$$

Now $\quad \dfrac{P_0 - P_s}{P_0} = \dfrac{wM}{Wm},$ $\quad$ or $\quad P_0 - P_s = P_0 \cdot \dfrac{wM}{Wm}$

or $(17.0 - P_s) = 17.0 \times \dfrac{3 \times 18}{50 \times 60} = 0.306$

or $P_s = 17.0 - 0.306 = 16.694$ mm.

3. At 0°C, the vapour pressure of water is 4·62 mm and a solu-
tion of 2·28 gm of $CaCl_2$ in 100 gm of water has a vapour pressure
of 4·584 mm. Calculate the degree of dissociation of $CaCl_2$.

Solution : By the question, we have

$$P_0 = 4.62 \text{ mm}, \qquad P_s = 4.584 \text{ mm},$$
$$w = 2.28 \text{ gm}, \qquad W = 100 \text{ gm},$$
$$M = 18, \qquad m = ?$$
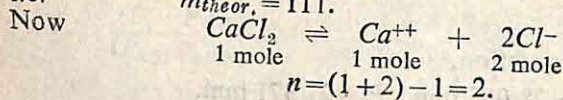
Now $\dfrac{P_0 - P_s}{P_0} = \dfrac{wM}{mW}$, or $\dfrac{4.62 - 4.584}{4.62} = \dfrac{2.28 \times 18}{m \times 100}$

or $m = \dfrac{4.62 \times 2.28 \times 18}{.036 \times 100} = 52.668$

i.e. $m_{observed} = 52.668$.

Theoretical molecular weight of $CaCl_2$
$$= 40 + 2 \times 35.5 = 111$$
i.e. $m_{theor.} = 111$.

Now $CaCl_2 \rightleftharpoons Ca^{++} + 2Cl^-$
            1 mole   1 mole   2 mole
$$n = (1 + 2) - 1 = 2.$$

$\therefore$ $\dfrac{m_{theor.}}{m_{obs.}} = 1 + 2\alpha$, or $\dfrac{111}{52.668} = 1 + 2\alpha$, or $2.1076 = 1 + 2\alpha$

or $2\alpha = 1.1076$, or $\alpha = \dfrac{1.1076}{2} = 0.5538$.

$\therefore$ Percentage dissociation = 55·38%.

4. Two liquids A and B form ideal solutions. At 300 K the
vapour pressure of a solution containing 1 mole of A and 3 moles of
B is 550 mm of Hg. At the same temperature if one more mole of B
is added to this solution, the vapour pressure of the solution
increases by 10 mm of Hg. Determine the vapour pressure of A and
B in their pure states.

Solution : Let P_A and P_B be the vapour pressures of pure liquids
A and B.

Let X_A and X_B be the mole fractions of A and B respectively.
Then,

$$X_A = \tfrac{1}{4} \text{ and } X_B = \tfrac{3}{4} \quad \text{(First mixture)}$$
$$X_A = \tfrac{1}{5} \text{ and } X_B = \tfrac{4}{5} \quad \text{(Second mixture)}$$

Let the vapour pressure of the mixture be P.

Then, $P = P_A \cdot X_A + P_B \cdot X_B$, or $550 = P_A \cdot \frac{1}{4} + P_B \cdot \frac{3}{4}$

or $\qquad\qquad\qquad P_A + 3P_B = 2200.$ .. (i)

Second mixture :

$$560 = P_A \cdot \tfrac{1}{5} + P_B \cdot \tfrac{4}{5}, \quad \text{or} \quad P_A + 4P_B = 2800. \qquad \text{.. (ii)}$$

Solving (i) and (ii), we get

$$P_A = 400 \text{ mm}, \quad P_B = 600 \text{ mm}.$$

Elevation of Boiling Point

The boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure. The boiling point of any liquid is fixed at a given pressure.

Whenever a non-volatile solute is dissolved in a solvent, the boiling point of the latter becomes higher. The difference of boiling points of a solution and the pure solvent is known as the elevation of boiling point of the solution. If T_0 be the boiling point of a pure solvent and T be the boiling point when a solute is dissolved in it, then elevation of boiling point, $\triangle T = (T - T_0)$.
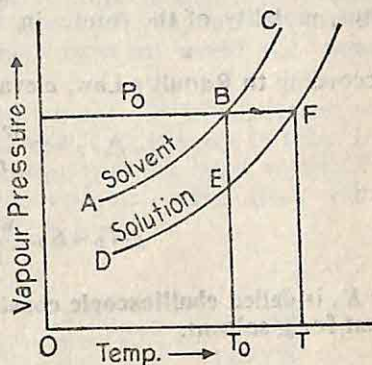
Cause of Elevation :

The boiling point of the solution is increased because of the lowering of vapour pressure on the dissolution of a non-volatile solute in the solvent.

The elevation of boiling point is directly proportional to the relative lowering of vapour pressure in dilute solution,

i.e.,
$$\triangle T \propto \frac{P_0 - P_s}{P_0}.$$

Raoult's Law of Elevation of Boiling Point

1. The elevation of boiling point of a solvent is proportional to the molar concentration of the solute in solution.

Thus, the elevation in boiling point of a 2 M solution of glucose be will twice the elevation of boiling point of a 1 M solution of glucose.

2. Equimolecular quantities of different substances dissolved in the same volume of a solvent register the same elevation in boiling point.

Thus, M solution of urea and M solution of glucose will have the same elevation in boiling point.

Relation between Elevation of Boiling Point and the Molecular Weight of the Solute :

Let w gm of a non-volatile and non-ionisable solute be dissolved in W gm of a solvent. Let m and M be the molecular weights of the solute and the solvent respectively.

Number of moles of solute $= w/m$.

$\therefore$ W gm of the solvent contains w/m moles of solute.

$\therefore$ 1000 gm of the solvent contains $\dfrac{w \times 1000}{m \times W}$ moles of solute.

Thus, molality of the solute in solution $= \dfrac{w \times 1000}{m \times W}$.

According to Raoult's Law, elevation of boiling point,

$$\triangle T_b \propto \dfrac{w \times 1000}{m \times W}$$

or

$$\triangle T_b = K_b. \ \dfrac{w \times 1000}{m \times W}$$

where K_b is called **ebullioscopic constant** or **boiling point elevation constant** for a solvent.

When $\dfrac{w}{m} = 1$ and $W = 1000$, then

$$\triangle T_b = K_b.$$

Thus, if one mole of the solute is dissolved in 1000 gm of the solvent the ebullioscopic constant is equal to the elevation in boiling point.

Relation between K_b and Latent Heat of Vaporisation :

Thermodynamically, it has been shown that

$$K_b = \dfrac{RT_0^2}{L \times 1000}$$

where, R is the gas constant and is equal to 1·987 calories, T_0 is the boiling point of the pure solvent on Kelvin scale and L is the latent heat of evaporation per gm of the solvent.

Determination of the Elevation in boiling point and hence the molecular weight of the non-volatile solute :

The molecular weight of a non-volatile solute is determined by using the formula :

$$m = \frac{K_b.\ w.\ 1000}{\triangle T_b.\ W}.$$

A known weight of the solute (w) is dissolved in a known weight of the solvent (W). A very sensitive thermometer called the Beckmann Thermometer is used to measure the boiling points. First of all, the boiling point of the pure solvent is determined. Then the boiling point of the solution is determined. The difference of the two gives the elevation in boiling point.

Two methods are usually adopted for the determination of the elevation of boiling point—

1. The Landsberger's Method—In this method, the solution is heated to boiling by passing into it the vapours of pure solvent. Heating with the help of vapours is done to avoid the danger of super-heating.

The flask A contains the pure solvent. It is connected through a delivery tube to a graduated tube B. At the top of tube B there is a hole to permit communication with the outer vessel C. The escaping vapours condense into a condenser. The inner tube B is provided with a thermometer.

A known weight of the solvent is taken in B. The vapour of the solvent is passed into it. The temperature of the solvent increases. When the temperature becomes constant, it is noted. This is the boiling point of the pure solvent.

A known weight of the solute is then put into the solvent and passing of vapour continued until the temperature becomes constant. This gives the boiling point of the solution. The volume of the solution in tube B is noted. From the density of the solvent, the mass of the solvent present in the

Boiling Liquid

Hole

Boiling Tube

To Condenser
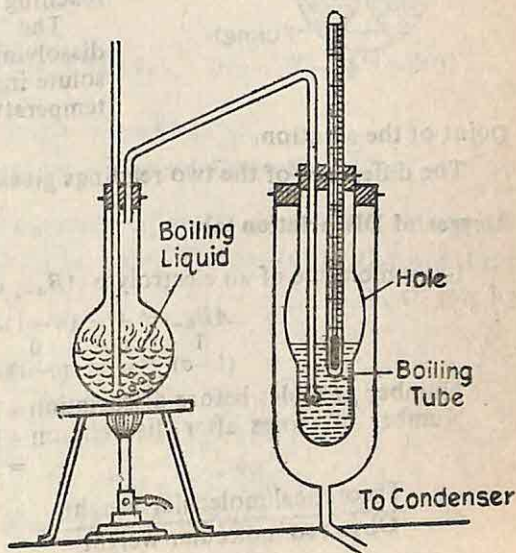
solution is found. The volume occupied by the solute is neglected.

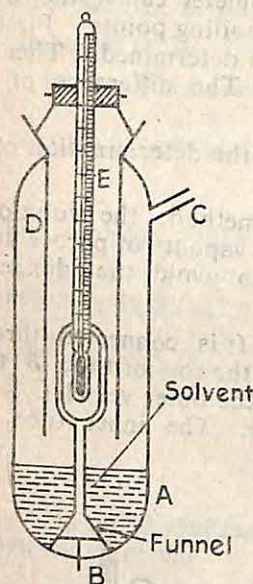The difference of the two readings gives the elevation in boiling point.

2. **Cottrell's Method**—This method is an improvement over the Landsberger's method. In this, the danger of superheating has been completely eliminated.

A known amount of the solvent is taken in the boiling tube A. An inverted funnel tube is placed in the boiling tube. The bubbles formed at the sealed platinum wire B force through this funnel a current of vapours over the bulb of the thermometer E placed above the surface of the liquid. The bulb is thus covered with a layer of boiling liquid in equilibrium with its vapour. The constant reading of the thermometer is noted. This gives the boiling point of the solvent.

The side tube C leads to a condenser and the sheath D prevents the cold condensate from reaching the thermometer.

The process is repeated by dissolving a known weight of the solute in the solvent. The constant temperature this time is the boiling point of the solution.

The difference of the two readings gives $\triangle T_b$.

Degree of Dissociation (α) :

Let a molecule of an electrolyte AB_{n-1} dissociate as,

$$AB_{n-1} \rightleftharpoons A^+ + (n-1)B^-$$

| 1 | 0 | 0 | (before dissociation) |
| $(1-\alpha)$ | α | $(n-1)\alpha$ | (after dissociation) |
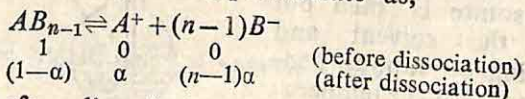
Number of moles before dissociation = 1.
Number of moles after dissociation = $1 - \alpha + \alpha + (n-1)\alpha$
$$= 1 + (n-1)\alpha.$$

$\therefore \quad \dfrac{\text{Theoretical molecular weight}}{\text{Observed molecular weight}}$

$$= \dfrac{\text{No. of moles after dissociation}}{\text{No. of moles before dissociation}}$$

i.e. $\dfrac{m_{theor.}}{m_{obs.}} = \dfrac{1+(n-1)\alpha}{1}$,   or $(n-1)\alpha = \dfrac{m_{theor.} - m_{obs.}}{m_{obs.}}$

or $\alpha = \dfrac{m_{theor.} - m_{obs.}}{(n-1)\,m_{obs.}}$.   Also $\alpha = \dfrac{\Delta T_{obs.} - \Delta T_{theor.}}{(n-1)\,\Delta T_{theor.}}$.

Solved Problems

1. The molal boiling point elevation constant K_b for carbon tetrachloride is 5·02 deg/mole. The boiling point of pure carbon tetrachloride is 76·8°C. Calculate the boiling point of a 1·0 molal solution of naphthalene ($C_{10}H_8$) in carbon tetrachloride.

Solution : By the question, we have,
$$K_b = 5·02 \text{ deg/mole,}$$
$$T_0 = 76·8°C, \quad T = ?$$

Molality of the solution $= \dfrac{w \times 1000}{m \times W} = 1·0$.

We know that, $\Delta T_b = K_b \dfrac{w \times 1000}{m \times W}$

or $T - T_0 = K_b \dfrac{w \times 1000}{m \times W} = 5·02 \times 1$,   or $T - 76·8 = 5·02$

or $T = 5·02 + 76·8 = 81·82°C$

i.e.   the boiling point of the solution $= 81·82°C$.

2. The molal elevation constant of water is 0·52°C. At what temperature will a solution of 5·6 gm of glucose ($C_6H_{12}O_6$) per litre boil ?   (P. U. 1976 A)

Solution : By the question, we have,
$$K_b = 0·52°C;$$

Boiling point of water, $T_0 = 100°C;$
$$w = 5·6 \text{ gm}, \quad m = 180,$$
$$W = 1000 \text{ ml} = 1000 \text{ gm.}$$

Now $\Delta T_b = T - T_0 = K_b \dfrac{w \times 1000}{m \times W}$

or $\quad T - 100 = \dfrac{0 \cdot 52 \times 5 \cdot 6 \times 1000}{180 \times 1000}$, $\quad$ or $\quad T - 100 = 0 \cdot 0161$

or $\qquad\qquad T = 100 + 0 \cdot 0161 = 100 \cdot 0161°C$

i.e. $\qquad\qquad$ B. P. of the solution $= 100 \cdot 0161°C$.

3. How much of cane-sugar (molecular weight $= 342$) must be dissolved in 300 ml of water so that the resulting solution has the same boiling point as a solution of 3 gm of urea (molecular weight $= 60$) in 100 ml of water ?

Solution : For cane-suger $\qquad\qquad$ For urea

$$\triangle T_b = K_b \dfrac{w \times 1000}{m \times W} \qquad\qquad \triangle T_b = K_b \dfrac{w \times 1000}{m \times W}$$

$$= K_b \dfrac{w \times 1000}{342 \times 300}. \qquad\qquad = K_b \dfrac{3 \times 1000}{60 \times 100}.$$

$\triangle T_b$ for both cane-sugar and urea is the same. Hence,

$$K_b \dfrac{w \times 1000}{342 \times 300} = K_b \dfrac{3 \times 1000}{60 \times 100}$$

or $\qquad w = \dfrac{342 \times 300 \times 3 \times 1000}{60 \times 100 \times 1000} = 51 \cdot 3$ gm.

4. A solution containing 0·5 gm of a substance dissolved in 42·0 gm of benzene boils at 80·175°C. Find the molecular weight of the substance if the boiling point of benzene is 80°C and its latent heat of vaporisation is 94 calories per gm. $\qquad$ **(Bhag. U. 1972 A)**

Solution : $\quad K_b = \dfrac{RT_0^2}{L \times 1000} = \dfrac{2 \times (80 + 273)^2}{94 \times 1000} = 2 \cdot 653.$

Now $\qquad m = \dfrac{K_b. \ w. \ 1000}{\triangle T_b. \ W} = \dfrac{2 \cdot 653 \times 0 \cdot 5 \times 1000}{(80 \cdot 175 - 80) \times 42}$

$$= \dfrac{2 \cdot 653 \times 0 \cdot 5 \times 1000}{0 \cdot 175 \times 42} = 180.$$

5. One gram of sucrose (molecular weight $= 342$) was dissolved in 105 gm of water. The solution was found to boil at 100·06°C at 760 mm pressure. How much water must be added to the solution so that the boiling point of the solution decreases to 100·045°C ?

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ **(Magadh U. 1976 A)**

Solution : By the question, we have

$$w = 1 \text{ gm}, \quad m = 342, \quad W = 105 \text{ gm}.$$
$$\therefore \quad T_0 = 100°C \text{ and } T = 100·06°C,$$
$$\therefore \quad \triangle T = (T - T_0) = (100·06 - 100) = 0·06°C.$$

Now $\quad K_b = \dfrac{\triangle T_b.\ m.\ W}{w \times 1000} = \dfrac{0·06 \times 342 \times 105}{1 \times 1000} = 2·155.$

Let the amount of water added to the solution be x gm. The b. p. of the new solution decreases to $100·045°C$.

Now, $\qquad w = 1 \text{ gm}, \quad W = (105 + x) \text{ gm}.$
$$\triangle T_b = 100·045 - 100 = 0·045°C, \quad K_b = 2·155.$$

$$\therefore \quad \triangle T_b = \frac{K_b.\ w.\ 1000}{m.\ W.}, \qquad \text{or} \qquad 0·045 = \frac{2·155 \times 1 \times 1000}{342 \times (105 + x)}$$

or $\qquad (105 + x) = \dfrac{2·155 \times 1 \times 1000}{342 \times 0·045} = 140.$

$$\therefore \quad x = 140 - 105 = 35 \text{ gm}.$$

6. The boiling point of a solution of $0·4388$ gm $NaCl$ in 100 gm of water is $102·07°C$. Calculate the apparent molecular weight of $NaCl$ and its degree of dissociation. (K_b for 100 gm water $= 5·2$)

Solution : By the question, we have

$$w = 0·4388 \text{ gm}, \qquad W = 100 \text{ gm},$$
$$T_0 = 100°C, \qquad T = 102·07°C.$$

Now, $\qquad m = \dfrac{K_b \times w \times 1000}{\triangle T_b \times W}.$

$\because \quad K_b$ for 100 gm water $= 5·2,$
$\therefore \quad K_b$ for 1000 gm water $= 0·52;$

$$\therefore \quad m = \frac{0·52 \times 0·4388 \times 1000}{(102·07 - 100) \times 100} = \frac{0·52 \times 0·4388 \times 10}{0·07} = 32·59.$$

Thus, the apparent molecular wt. of $NaCl = 32·59$. $NaCl$ dissociates as,
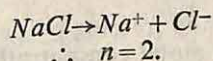
$$NaCl \rightarrow Na^+ + Cl^-$$
$$\therefore \quad n = 2.$$

Theoretical molecular weight $= 58·5.$

Let the degree of dissociation of $NaCl$ be α. Then,

$$\alpha = \frac{(\text{Theoretical mole.wt.}) - (\text{Observed mole. wt.})}{(n - 1)\ \text{observed mole. wt.}}$$

$$= \frac{58·5 - 32·59}{(2 - 1) \times 32·59} = \frac{25·91}{32·59} = 0·79 \text{ or } 79\%.$$

Depression of Freezing Point
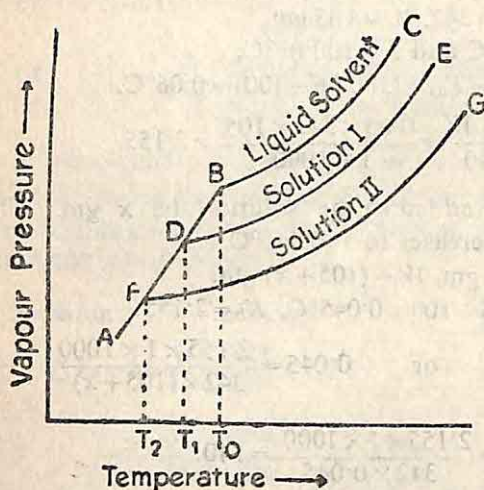
When a liquid solvent is cooled, a temperature is reached when solid solvent begins to separate from the liquid solvent. This temperature is the **freezing point** of the solvent. This is the temperature at which the solid solvent is in equilibrium with the liquid solvent and hence they have the same vapour pressure.

When a solute is dissolved in the solvent, the freezing point of the solvent decreases. This is called **depression in freezing point**. Thus, if T_0 is the freezing point of the pure solvent and T_1 is the freezing point of a solution obtained by dissolving some non-volatile and non-ionisable solute in the solvent, then

Depression in freezing point $= (T_0 - T_1) = \triangle T_f$.

Cause of Depression in Freezing Point :

At atmospheric pressure, a pure solvent freezes at a definite temperature. At this temperature, the vapour pressure of the solvent is equal to the vapour pressure of its solid. When a solute is dissolved in the solvent, the vapour pressure of the solvent decreases. Hence, temperature decreases in order that the vapour pressure of the solid may be equal to that of the solvent. This is why the freezing point of a solvent decreases when a solute is dissolved in it.

Raoult's Law of the Depression in Freezing Point :

The laws propounded by Raoult regarding the depression in freezing point are :

1. The depression in the freezing point of a solvent by a dissolved solute is proportional to molal concentration of the dissolved solute.

$$\triangle T_f \propto C_m, \quad \text{or} \quad \triangle T_f = K_f C_m.$$

2. Equimolecular quantities of different solutes dissolved in the same quantity of a particular solvent, depress the freezing point to the same extent.

Thus, N/10 solution of glucose and N/10 solution of urea will have the same freezing point.

Limitations of Raoult's Laws—(i) They hold good only for non-volatile and non-ionisable solutes.

(ii) The solutions must be very dilute.

(iii) The solute should not suffer any association or dissociation in solution.

(iv) The process of freezing should occur with the solvent only, not with the solute.

Relation between Depression of Freezing Point and the Molecular Weight of the Solute :

Let w gm of a solute be dissolved in W gm of a solvent. The molecular weight of the solute is m. Hence, the number of moles of solute $= w/m$.

Now, $\because$ W gm of solvent contains w/m moles of solute,

$\therefore$ 1000 gm of solvent contains $\dfrac{w \times 1000}{m \times W}$ moles of solute

i.e. molal concentration (C_m) of solution $= \dfrac{w \times 1000}{m \times W}$.

If $\triangle T_f$ be the depression of the freezing point, then

$$\triangle T_f = K_f \, \frac{w \times 1000}{m \times W}$$

where, K_f is a constant known as the **molal depression constant** or the **cryoscopic constant**.

When $w = m$ and $W = 1000$, then $K_f = \triangle T_f$, that is, **the depression in freezing point produced on dissolving 1 gm mole of solute in 1000 gm of the solvent, is known as the molal depression constant of the solvent.**

The K_f values for 1000 gm and 100 gm of some solvents are noted below—

Solvent	Freezing point	K_f (1000 gm)	K_f (100 gm)
Water	0°C	1·86	18·6
Benzene	5°C	5·12	51·2
Acetic acid	17°C	3·90	39·0
Phenol	40°C	7·27	72·7
Formic acid	8°C	2·8	28·0
Camphor	178°C	37·7	377·0

Relation between K_f and Latent heat of fusion (L) :

Thermodynamically, it has been established that

$$K_f = \frac{RT_0^2}{1000 \times L}$$

INTR. CH-20

where K_f = molal depression constant,
R = gas constant = 0·02 cal/mole,
T_0 = freezing point of the solvent on Kelvin scale, and
L = latent heat of fusion per gm of the solvent.

Experimental determination of Depression of the Freezing Point :

The Beckmann Method—The apparatus used is shown in the figure. It consists of a freezing tube A containing the solvent. It is fitted with a side tube B through which a known weight of the solute is inserted. The tube A is fitted with a Beckmann thermometer and a stirrer and is surrounded by an air-jacket. The latter prevents rapid cooling of the contents in tube A. The whole system is placed in a bigger vessel containing the freezing mixture.
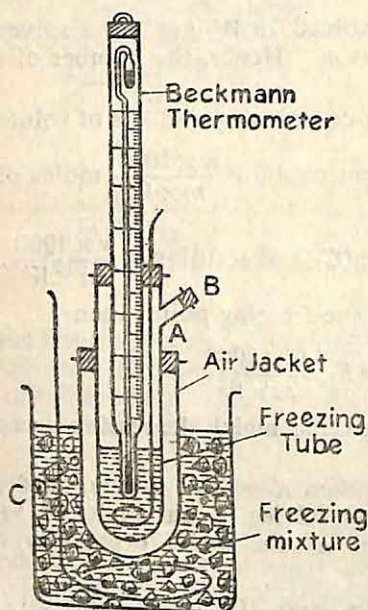
After setting the apparatus the freezing point of a known weight of the solvent is first determined. The solvent is slowly cooled by about 0·5° below its freezing point. It is then stirred vigorously when the temperature begins to rise. The rise in temperature continues up to its freezing temperature. The temperature then becomes static which is noted.

A known weight of solute whose molecular weight is to be determined, is then put into the tube A through the side. It is completely dissolved. The freezing point of the solution is determined as before. The difference of the two readings gives the depression of the freezing point.

The molecular weight of the solute is now calculated by using the formula—

$$m = K_f . \frac{w \times 1000}{\triangle T_f \times W}$$

where m = molecular weight of solute,
             K_f = molal depression constant,
             w = weight of the solute,
             $\triangle T_f$ = depression in freezing point,
             W = weight of the solvent.

Numericals

1. A solution containing 62·5 g of a nonvolatile solute per 1000 g of water has a freezing point 1·6°C less than that of water. Calculate the molecular mass of the solute.

$$(K_f = 1·86°C/mol/kg \text{ of water})$$

Solution : By the question, we have
$$w = 62·5 \text{ g}, \quad W = 1000 \text{ g},$$
$$\triangle T_f = 1·6°C, \quad K_f = 1·86.$$

Now $m = K_f . \dfrac{w \times 1000}{\triangle T_f \times W}$

$$= 1·86 \times \frac{62·5 \times 1000}{1·6 \times 1000} = 1·1625 \times 62·5 = 72·2.$$

2. What is the molecular weight of a substance of a solution of 3·00g in 200g in benzene freezes at 4·98°C ? (Freezing point of benzene = 5·5°C, and K_f for 1000 g benzene = 5·12.)

Solution : By the question, we have,
$$w = 3·00 \text{ g}, \quad W = 200 \text{ g}$$
$$\triangle T_f = T_0 - T = 5·5 - 4·98 = 0·52°C,$$
$$K_f = 5·12.$$

Now, molecular weight, $m = K_f \dfrac{w \times 1000}{\triangle T_f \times W}$

$$= 5·12 \times \frac{3 \times 1000}{0·52 \times 200} = 147·6.$$

3. A solution contains 5 g of glucose and 5 g of urea in 800 g of water. (a) Calculate the freezing point of the solution. (b) How much water would have to be evaporated in order that the solution have a freezing point of $-0·82°C$?

Solution : (a) We know that,
$$\triangle T_f = K_f . C_m,$$
Molecular weight of glucose $(C_6H_{12}O_6) = 180$,
Molecular weight of urea $(NH_2CONH_2) = 60$.
∴   No. of moles of glucose $= \frac{5}{180} = 1/36$,
∴   No. of moles of urea $= 5/60 = 1/12$.
∴   Total number of moles $= \frac{1}{36} + \frac{1}{12} = \frac{1}{9}.$

$\therefore$ Molal concentration $(C_m) = \dfrac{1}{9} \times \dfrac{1000}{800} = 5/36.$

$\therefore \quad \triangle T_f = K_f. \ C_m = 1\cdot86 \times 5/36 = 0\cdot258$
i.e., the freezing point of solution $= -0\cdot258.$

(b) Suppose x is the gm of water evaporated. Then, weight of water $= (800 - x)$ g.

$\therefore$ Molal concentration, $C_m = \dfrac{1}{9} \times \dfrac{1000}{(800-x)}$

$\therefore \quad \triangle T_f = 1\cdot86 \times \dfrac{1}{9} \times \dfrac{1000}{(800-x)}$

or $\quad 0\cdot82 = \dfrac{1\cdot86-1000}{9\times(800-x)},$ or $\quad x = 548$ g.

4. When $0\cdot82$ g of naphthalene $(C_{10}H_8)$ is dissolved in 40 g of benzene, the freezing point of benzene is lowered by $0\cdot312^\circ$C. When $0\cdot4$ g of another substance is dissolved in 55 g of the same solvent, the observed depression in freezing point is $0\cdot05^\circ$C. Find the molecular weight of the second substance. **(P. U. 1974 A)**

Solution : By the question, we have
$$w = 0\cdot82 \text{ g}, \quad W = 40 \text{ g},$$
$$m = \text{molecular weight of } C_{10}H_8 = 128,$$
$$\triangle T_f = 0\cdot312^\circ\text{C}, \quad K_f = ?$$

$$K_f = \frac{m \times \triangle T_f \times W}{w \times 1000} = \frac{128 \times 0\cdot312 \times 40}{0\cdot82 \times 1000}$$

$$= \frac{1597\cdot44}{820} = 1\cdot948.$$

For the second substance :

$$m = ?, \quad w = 0\cdot4 \text{ g}, \quad W = 55 \text{ g}, \quad \triangle T_f = 0\cdot05^\circ\text{C}.$$

Now $\quad m = K_f. \dfrac{w \times 1000}{\triangle T_f \times W}$

$$= 1\cdot948 \times \frac{0\cdot4 \times 1000}{0\cdot05 \times 55} = \frac{779\cdot2}{2\cdot75} = 283\cdot3.$$

Abnormal depression in freezing point :

When the solute is an electrolyte, it ionises in solution. The number of particles in solution thus increases. Hence, such a solution exhibits abnormal depression in freezing point.

Let us consider the ionisation of AB_{n-1} molecule into n molecules.

$$AB_{n-1} \rightarrow A^+ + (n-1)B^-$$

1 mole	0	0	(before ionisation)
$(1-\alpha)$	α	$(n-1)\alpha$	(after ionisation)
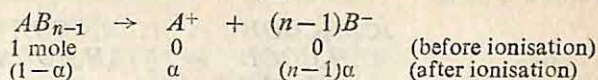
Number of molecules before ionisation $=1$.
Number of molecules after ionisation $=(1-\alpha)+\alpha+(n-1)\alpha$
$$=1+(n-1)\alpha.$$

We know that $\triangle T_f \propto$ number of moles.

Hence, $$\frac{(\triangle T_f)_{obs.}}{(\triangle T_f)_{th.}} = \frac{1+(n-1)\alpha}{1}.$$

But $\triangle T_f = K_f \cdot \dfrac{w \times 1000}{m \times W}$. $\quad \because \quad K_f$, w and W are constants,

$$\therefore \quad \triangle T_f \propto \frac{1}{m}. \qquad \therefore \quad \frac{m_{th.}}{m_{obs.}} = \frac{1+(n-1)\alpha}{1}$$

or $\dfrac{m_{th.}-m_{obs.}}{m_{obs.}} = (n-1)\alpha;$ $\therefore$ $\alpha = \dfrac{m_{th.}-m_{obs.}}{(n-1)m_{obs.}}.$

5. A solution containing 1·26 g $NaCl$ in 50 g of water freezes at $-1\cdot53°C$. Calculate the degree of dissociation of $NaCl$, if K_f for 100 g of water is 18·6.

Solution : K_f for 100 g water $= 18\cdot6$.
$\therefore$ K_f for 1000 g water $= 1\cdot86$, $w = 1\cdot26$ g, $W = 50$ g,
$\triangle T_f = 1\cdot53°C$, $m = ?$

$$m = K_f \frac{w \times 1000}{\triangle T_f \times W}$$

or $m = 1\cdot86 \times \dfrac{1\cdot26 \times 1000}{1\cdot53 \times 50} = 30\cdot635$ i.e. $m_{obs.} = 30\cdot635$.

$\therefore$ $m_{th.} = 58\cdot5$, $NaCl$ ionises as,
$$NaCl \rightarrow Na^+ + Cl^-; \qquad \therefore \quad n = 2.$$

Now, $\alpha = \dfrac{m_{th.}-m_{obs.}}{(n-1)m_{obs.}} = \dfrac{58\cdot5-30\cdot635}{(2-1) \times 30\cdot635} = 0\cdot909$
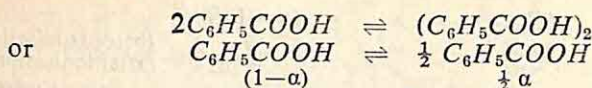
i.e. $\alpha = 90\cdot9\%$.

6. A solution containing 0·2965 gm of benzoic acid (C_6H_5COOH) in 20·27 gm of benzene was found to freeze at 0·317° below the freezing point of the solvent. Calculate (i) the apparent molecular weight of the acid, (ii) the degree of association. Given, $K_f = 5\cdot12$.

(I. I. T. Pattern)

Solution : The association of benzoic acid in benzene may be

represented as

$$2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$
or
$$C_6H_5COOH \rightleftharpoons \tfrac{1}{2} C_6H_5COOH$$
$$(1-\alpha) \qquad\qquad \tfrac{1}{2}\,\alpha$$

α is the degree of association.

Total number of particles after association $= 1 - \alpha + \alpha/2 = (1 - \alpha/2)$.
Normal molecular weight of benzoic acid $= 122$.
Let observed molecular weight of benzoic acid be m.

$$\therefore \quad m = \frac{K_f.\ w.\ 1000}{\triangle T_f.\ W}.$$

By the question, we have $K_f = 5\cdot12$,
    $w = 0\cdot2965$ gm, $\triangle T_f = 0\cdot317$, $W = 20\cdot27$ gm.

$$\therefore \quad m = \frac{5\cdot12 \times 0\cdot2965 \times 1000}{0\cdot317 \times 20\cdot27} = 236\cdot2.$$

Now, $\dfrac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$

$$= \frac{\text{No. of particles after association}}{\text{No. of particles before association}}$$

or $\quad \dfrac{122}{236\cdot2} = \dfrac{1 - \alpha/2}{1}$, or $\alpha = 0\cdot97$, $\therefore$ % association $= 97\%$.

Osmosis and Osmotic Pressure

Osmosis is an important colligative property. It was first reported by Abbe Nollet in 1748. It was observed that when the solution of a solute was separated from the pure solvent by a porous membrane, the solvent was found to pass spontaneously into the solution. This process is called osmosis. Thus, **the spontaneous flow of a solvent into the solution or from a dilute to a concentrated solution through a semi-permeable membrane is known as Osmosis.**

In osmosis, only the flow of solvent takes place.

The function of the semi-permeable membrane is to allow the solvent molecules only and not the solute molecules through it. Examples of semi-permeable membranes are animal membranes, cellulose, parchment paper, a film of cupric ferrocyanide etc.

Phenomena of Osmosis : (i) Swelling and Contraction of an Egg— When a boiled egg with its shell removed is put into a dilute solution of HCl, it swells up in size. This is because the water from outside enters the interior of the egg through the semi-permeable skin by the process of osmosis.

When the same egg is placed in a *NaCl* solution, it contracts in size. This is because the flow of water takes place from the interior of the egg to the solution side.

(ii) Abbe Nollet's Experiment—The end of a thistle funnel is wrapped by an animal membrane. It is partially filled with a concentrated solution of sugar and immersed in a beaker containing pure water. The process of osmosis starts. The water from the beaker slowly passes through the membrane to the sugar solution. As a result, the level of sugar solution rises in the thistle tube until it reaches a definite height. The difference in levels of the sugar solution and the water is equal to the hydrostatic pressure set up. This is the **osmotic pressure** of the solution.
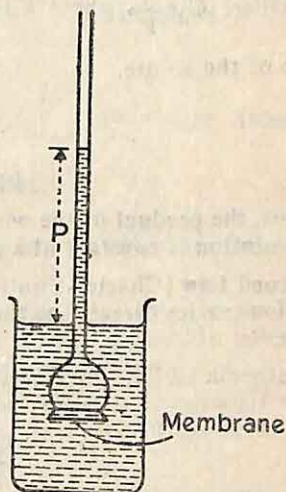
Membrane

Osmotic Pressure—The osmotic pressure of a solution is defined as the mechanical pressure which must be applied on a solution to prevent the passage of solvent into the solution through a semi-permeable membrane.

The osmotic pressure is thus a measure of difference of pressure between the solvent and the solution. It does not depend upon the nature of the semi-permeable membrane. It, however, depends on the nature of the solvent and the solute.

Cause of Osmosis—We know that the vapour pressure of a pure solvent is greater than that of the same solvent in any of its solution. When a pure solvent is separated from its solution through a semi-permeable membrane, a difference in vapour pressure exists on the two sides. Osmosis sets in because diffusion always takes place from a region of higher pressure to that of lower pressure.

Laws of Osmotic Pressure

In 1887 Van't Hoff established the existence of a close resemblance between a solute in the gaseous state and its dilute solution. He propounded a theory, known as the **Theory of dilute solutions.** According to this theory, **the osmotic pressure of a dilute solution is equal to that pressure which the solute itself would exert when in the gaseous state having volume equal to that of the dilute solution.**

Later on, Van't Hoff proposed some laws regarding the behaviour

of dilute solutions—

First Law (Boyle-Van't Hoff's Law)—The osmotic pressure of a dilute solution is directly proportional to its concentration at constant temperature. Mathematically,

$$P \propto C, \text{ when } T \text{ is constant.}$$

Further, $C \propto \dfrac{1}{V}$, where V is the volume of solution containing 1 mole of the solute.

$$\therefore \quad P \propto \frac{1}{V}$$

or
$$PV = \text{constant.} \qquad \qquad .. \text{ (i)}$$

Thus, the product of the osmotic pressure and the volume of a dilute solution is constant at a given temperature.

Second Law (Charles-Van't Hoff's Law)—The osmotic pressure of a solution varies directly as the Kelvin temperature at a given concentration.

Mathematically, $P \propto T$, when C is constant
or $P = kT$, where k is a constant
or
$$\frac{P}{T} = k. \qquad \qquad .. \text{ (ii)}$$

Equations (i) and (ii) are similar to Boyle's Law and Charles' Law respectively for gases. The only difference that exists is that the osmotic pressure (P) is taken for the gas pressure.

Third Law (Avogadro-Van't Hoff's Law)—According to this law, equal volumes of all solutions having the same osmotic pressure and temperature contain the same number of molecules.

For solution I, $P_1 V_1 = n_1 R T_1$
For solution II, $P_2 V_2 = n_2 R T_2$.
When $P_1 = P_2$, $V_1 = V_2$ and $T_1 = T_2$, then $n_1 = n_2$.

Thus, solute molecules in solution obey Avogadro's hypothesis.

From the results of these investigations Van't Hoff was able to draw a similarity between the properties of solution and the properties of gases.

Combined Form of the First and the Second Laws : Van't Hoff combined equations (i) and (ii) and suggested the relation

$$PV = RT,$$

where R is a constant, V is the volume of the solution containing 1 mole of the solute. If n moles of a solute are dissolved in volume V of the solution, the above equation becomes

$$PV = nRT.$$

Value of R—R in equation, $PV = RT$ is a constant, known as the solution constant. The numerical value of the solution constant is the same as that of the gas constant.

Isotonic Solutions—Two solutions having the same osmotic pressure are called isotonic solutions. Thus, when two isotonic solutions are kept in contact with each other through a semi-permeable membrane, there is no osmosis from either of them. This is because the isotonic solutions have the same molar concentration and the the same vapour pressure.

$\dfrac{M}{10}$ solution of urea and $\dfrac{M}{10}$ solution of glucose are isotonic because their molar concentration is the same.

$\dfrac{M}{10}$ solution of glucose and $\dfrac{M}{10}$ solution of $NaCl$ are not isotonic. This is because although M/10 solution of glucose contains 1/10 mole of glucose per litre, a litre of M/10 $NaCl$ solution contains more than 1/10 mole on account of ionisation of $NaCl$.

Hypertonic Solution—A solution is said to be hypertonic with respect to the other when the osmotic pressure of the former is higher than that of the latter.

Hypotonic Solution—A solution is said to be hypotonic with respect to the other when the osmotic pressure of the former is less than that of the latter.

Relation between Osmotic pressure of solution and the molecular weight of solute :

Let a solution containing w g of a solute produce an osmotic pressure P. Then,

$$PV = nRT$$

or $\quad PV = w/m \; RT$, where m = molecular weight of solute

or

$$m = \frac{w.RT}{PV}$$

where V = volume of solution containing w gm of the solute,

$\qquad R = 0.0821$,
$\qquad P$ = osmotic pressure in atmosphere,
$\qquad T$ = absolute temperature.

Abnormal Osmotic Pressure—In order to account for the abnormal behaviour of electrolytes in solution, Van't Hoff introduced the factor 'i', known as the Van't Hoff factor. This factor is defined as, the ratio of the colligative effect produced by a definite concentration

of the electrolyte divided by the effect observed for the same concentration of a non-electrolyte.

i.e., $$i = \frac{\triangle T_b}{(\triangle T_b)_o} = \frac{\triangle T_f}{(\triangle T_f)_o} = \frac{P}{(P)_o} = \frac{(P_o - P)}{(P_o - P)_o}.$$

The subscript 'o' in the denominator indicates the value for the non-electrolyte.

For solutions of electrolytes,

$$P_o - P = i \ (P_o - P)_o = iP_o . \ X_B$$

$$X_B = \text{mole fraction of solute}$$
$$P_o = \text{vapour pressur of seolvent}$$
$$\triangle T_f = i(\triangle T_f)_o = iK_f . \ m$$
$$\triangle T_b = i(\triangle T_b)_o = iK_b m$$

Osmotic pressure, $$P = i(P)_o = i \frac{nRT}{V}.$$

Degree of Dissociation—The fraction of the total number of molecules which dissociates into ions is called the degree of dissociation (α).

$$A_x B_y \ \rightleftharpoons \ xA^+ \ + \ yB^-$$
$$\begin{array}{cccc} m & & 0 & 0 \\ m(1-\alpha) & & mx\alpha & my\alpha \end{array}$$
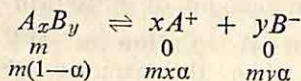
Total number of moles before dissociation $= m$

Total number of moles after dissociation $= m(1-\alpha) + mx\alpha + my\alpha$
$$= m[1 + \alpha(x + y - 1)].$$

Let $x + y = n$.

$\therefore$ Total number of moles after dissociation
$$= m[1 + \alpha(n-1)].$$

$\therefore \quad \dfrac{P}{(P)_o} = \dfrac{m[1 + \alpha(n-1)]}{m}, \quad \text{or} \quad i = [1 + \alpha(n-1)]$

or $\quad i - 1 = \alpha(n-1), \quad$ or $\quad \alpha = \dfrac{i-1}{(n-1)}.$

Measurement of Osmotic Pressure

1. Berkeley and Hartley Method—This is an accurate method for measuring the osmotic pressure of a solution, The outline of the apparatus used is shown in given figure. The solution, of which the osmotic pressure is to be determined is placed in vessel A made of gun metal alloy. This vessel is fitted with a water-tight piston. By putting known weights on the piston, the desired pressure can be exerted on the surface of the solution. A porous tube B is tightly joined to the vessel A. On the sides of the tube B a thin layer of

copper ferrocyanide is deposited. This serves as a semi-permeable membrane. Tube B is filled with the solvent and is provided with a capillary tube T on one side of it.
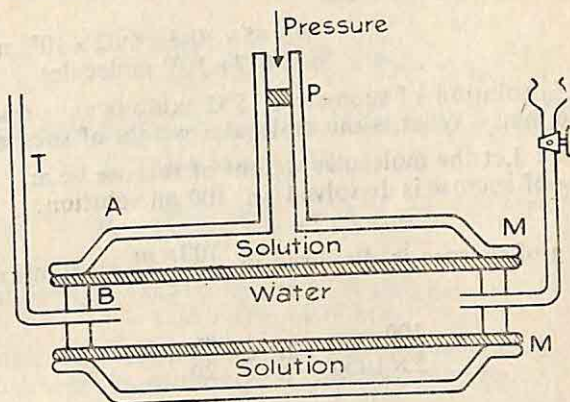
Due to osmosis, the level of liquid in the capillary falls, [but by applying a suitable pressure on the piston, it is brought back to its original position. This pressure is taken as the osmotic pressure of the solution.

Advantages of the Method—(i) As equilibrium is established soon, it is less time-consuming.

(ii) There is no possibility of the semi-permeable membrane being broken as it is under equal pressure on both sides of it.

(iii) The concentration of the solution does not change.

(iv) The apparatus is portable.

Solved Problems

1. The osmotic pressure of a sugar solution at 24°C is 2·51 atmospheric pressure. What is the concentration of solution in mole per litre ?

Solution : Let the number of moles per litre be n.

$$\therefore \quad PV = nRT$$

or $2\cdot51 \times 1 = n \times 0\cdot082 \times (273+24)$,   or $2\cdot51 = n \times 0\cdot082 \times 297$

or

$$n = \frac{2\cdot51}{0\cdot082 \times 297} = 0\cdot1029.$$

2. How many molecules of urea must be added to 10 ml of water at 10°C if an osmotic pressure of 0·8 atm. is to be established ?

Solution : $V = 10$ ml $= 0\cdot01$ litre,

$P = 0\cdot8$ atm, $R = 0\cdot082$, $T = 273 + 10 = 283$ K.

$$PV = nRT$$

Now

or $0.8 \times 0.01 = n \times 0.082 \times 283$

or $n = \dfrac{0.8 \times 0.01}{0\,082 \times 283} = 3.45 \times 10^{-4}$ moles.

$$= 3.45 \times 10^{-4} \times 6.02 \times 10^{23} \text{ molecules}$$
$$= 2.077 \times 10^{20} \text{ molecules.}$$

3. A 2% solution of sucrose at 15°C exhibits an osmotic pressure of 1016 mm. What is the molecular weight of sucrose ?

Solution : Let the molecular weight of sucrose be m.

$\because$ 2 g of sucrose is dissolved in 100 ml solution,

$\therefore$ m g of sucrose is dissolved in $\dfrac{100 \times m}{2}$ ml solution

$$= \dfrac{100 \times m}{2 \times 1000} \text{ litre} = \dfrac{m}{20} \text{ litre.}$$

$$\therefore \quad V = \dfrac{m}{20}.$$

Now $P = 1016 \text{ mm} = \dfrac{1016}{760} \text{ atm.}$

$\because PV = RT,$ $\therefore$ $\dfrac{1016}{760} \times \dfrac{m}{20} = 0.082 \times 288$

or $m = \dfrac{0.082 \times 288 \times 760 \times 20}{1016} = 353.3.$

4. A solution contains 0.40% urea (molecular weight = 60) and 3.42% sucrose dissolved in it. Calculate the osmotic pressure of the solution at 27°C.

Solution : $\because$ 40 g urea is dissolved in 100 ml solution,

$\therefore$ 60 g urea is dissolved in $\dfrac{100 \times 60}{0.40}$ ml solution

$$= \dfrac{100 \times 60}{0.40 \times 1000} \text{ litre} = \dfrac{3}{0.20} \text{ litre.}$$

Let pressure exerted by urea molecules be P_1.

$$\therefore \quad P_1 \times \dfrac{3}{0.20} = 0.082 \times 300$$

or $P_1 = \dfrac{.082 \times 300 \times .20}{3} = 1.64 \text{ atm.}$

Similarly, $\because$ 3·42 g sucrose is dissolved in 100 ml solution,

$\therefore$ 342 g sucrose is dissolved in $\dfrac{100 \times 342}{3\cdot 42}$ ml solution

$$= \frac{100 \times 342}{3\cdot 42 \times 1000} = 10 \text{ litre.}$$

Let the pressure exerted by sucrose molecule be P_2.

Then, $\qquad P_2 \times 10 = 0\cdot 082 \times 300$

or $\qquad\qquad P_2 = \dfrac{\cdot 082 \times 300}{10} = 2\cdot 46 \text{ atm.}$

$\therefore$ Total pressure exerted by the solution
$$= 1\cdot 64 + 2\cdot 46 = 4\cdot 10 \text{ atm.}$$

5. Calculate the concentration of a solution of glucose which is isotonic with a solution containing 6 g of urea per litre.

Solution : 6 g urea $= \frac{6}{60} = 0\cdot 1$ mole per litre.

Thus, $\qquad V = 1$ litre, $n = 0\cdot 1$, $\quad \therefore \quad P \times 1 = 0\cdot 1 \times R \times T$

or $\qquad\qquad\qquad P = 0\cdot 1 \times R \times T.$ .. (i)

Let the concentration of glucose solution be n_1 moles per litre.

Hence, $\qquad\qquad P \times 1 = n_1 \times RT.$ .. (ii)

$\therefore \quad n_1 \times R \times T = 0\cdot 1 \times R \times T$, or $\quad n_1 = 0\cdot 1$ mole

i.e., concentration of glucose solution
$$= 0\cdot 1 \text{ mole per litre} = 0\cdot 1 \times 180 \text{ g per litre} = 18 \text{ g per litre.}$$

6. 3·58 g of *NaCl* was dissolved in 120 g of water at 77°C. The osmotic pressure of the solution was found to be 2000 cm. Calculate the degree of dissociation of the dissolved salt.

Solution : Let the theoretical osmotic pressure be P_{th}.

$$PV = nRT$$

or $\qquad\qquad P_{th.} \times \dfrac{120}{1000} = \dfrac{3\cdot 58}{58\cdot 5} \times 0\cdot 082 \times 350$

or $\qquad\qquad P_{th.} = \dfrac{3\cdot 58 \times 0\cdot 082 \times 350 \times 1000}{58\cdot 5 \times 120} = 14\cdot 64 \text{ atm.}$

$\because \qquad\qquad P_{obs.} = \dfrac{2000}{76} \text{ atm} = 26\cdot 32 \text{ atm,}$

$\therefore \qquad\qquad \alpha = \dfrac{P_{obs.} - P_{th.}}{(n-1)P_{th.}} = \dfrac{26\cdot 32 - 14\cdot 64}{14\cdot 64}$

$$= 0\cdot 7978 \qquad \text{or} \qquad 79\cdot 78\%.$$

7. The osmotic pressure of a solution containing 32·4 g of sucrose per litre was found to be 2·43 atm. at 0°C. What would be the osmotic pressure at 20°C of a solution containing 42 g of sucrose per litre ?

Solution :

∵   32·4 g sucrose is dissolved in 1 litre,

∴   342 g sucrose is dissolved in $\dfrac{342}{32·4}$ litre

i.e.,   volume containing 4 mole of sucrose $= \dfrac{342}{32·4}$ litre

i.e., $V = \dfrac{342}{32·4}$ litre, $P = 2·43$ atm, $T = 273$ K

Now $PV = RT.$

∴ $R = \dfrac{PV}{T} = \dfrac{2·43 \times 342}{273 \times 32·4} = 0·094$ litre atm deg^{-1}.

For the second solution :

∵   42 g sucrose is dissolved in 1 litre,

∴   342 g sucrose is dissolved in $\dfrac{342}{42}$ litre

i.e., $V = \dfrac{342}{42}$ litre, $P = ?$, $T = 293$ K

Now $PV = RT$

or $P = \dfrac{RT}{V} = \dfrac{0·094 \times 293 \times 42}{342} = 3·38$ atm.

Questions

Long Answer Type :

1. State and explain Raoult's Law of the lowering of vapour pressure.

2. What do you mean by relative lowering of vapour pressure of a solvent ? Deduce an expression for the relationship between the molecular weight of a solute and the relative lowering of vapour pressure.

3. Describe an experiment to determine the lowering of vapour pressure of a solvent when a non-volatile solute is dissolved in it.

4. Explain how Raoult's Law can be used for determining the molecular weight of a dissolved non-volatile substance.

5. What is meant by elevation of boiling point ? How is it related to the molecular weight of a solute ?

6. What is molal elevation constant ? Describe Landsberger's method for determining the elevation of boiling point of water on dissolving a non-volateil solute in it.

7. What is meant by cryoscopic constant ? Explain how the depression of a solvent may be used to determine the molecular weight of the dissolved substance.

8. State the laws of osmotic pressure. Explain how the osmotic pressure is analogous to gas pressure. How can the molecular weight of a substance in solution be determined from its osmotic pressure ?

9. Write short notes on :

(i) Semi-permeable membrane, (ii) Osmosis, (iii) Osmotic pressure, (iv) Isotonic solution, (v) Hypertonic solution, (vi) Hypotonic solution, (vii) Van't Hoff Theory of dilute solutions.

Short Answer Type :

1. Vapour pressure lowering is a colligative property, i.e., it is a property which depends only on the number of solute particles in solution and not on the nature of these particles. Explain.

2. Will the normal boiling point of an aqueous solution and pure water be the same ? Why ?

3. How does the vapour pressure lowering affect the freezing point of the solution ?

4. Under what conditions does water boil at ordinary temperature ?

5. Why is the vapour pressure of a solvent lowered by dissolving a solute in it ?

6. Which of the following will have a higher vapour pressure ?

M/10 solution of urea or M/10 solution of $NaCl$.

Objective Questions

1. A small amount of urea is dissolved in water. The vapour pressure of the solution will (i) increase (ii) decrease (iii) remain constant (iv) be none of these.

2. The lowering in vapour pressure of M/10 solution of urea as compared to M/10 solution of KCl would be

(i) same (ii) higher (iii) lower (iv) half.

3. Lowering in vapour pressure will be

(i) 0·1 M Na_2SO_4 (ii) 0·1 M $NaCl$ (iii) 0·1 M urea.   **(Bihar PMDT, 1979)**

4. Lowering in vapour pressure is (i) a colligative property (ii) an extensive property (iii) an intensive property (iv) a fundamental property.

5. Whenever a non-volatile solute is added to a solvent

(i) the vapour pressure of the solvent remains unchanged

(ii) the vapour pressure of the solvent increases

(iii) the vapour pressure of the solvent is lowered

(iv) the volume of the solution increases.

6. The relative lowering in vapour pressure of a solvent is equal to the mole fraction of the solute dissolved in it. This statement is known as

(i) Boyle's Law (ii) Raoult's Law (iii) Charles' Law.

7. 0·1 M solution of urea and 0·1 M solution of glucose will have

(i) same vapour presure (ii) approximately the same vapour pressure (iii) different vapour pressures.

8. Which of the following produces abnormal lowering of vapour pressure in water.

(i) urea (ii) sucrose (iii) sodium chloride (iv) fructose.

9. Two solutions A and B have the same osmotic pressure. Such solutions are called (i) Hypotonic (ii) Hypertonic (iii) Isotonic (iv) conjugate.

10. Which of the following is an additive property ?

(i) lowering of vapour pressure (ii) elevation of boiling point (iii) mass (iv) none.

11. The relative lowering in vapour pressure of a solution is

(i) inversely proportional to the osmotic pressure
(ii) directly proportional to its osmotic pressure
(iii) equal to its osmotic pressure
(iv) none of these.

12. The lowering in vapour pressure depends on

(i) number of solvent molecules
(ii) total number of molecules in solution
(iii) number of solute particles in solution
(iv) weight of solute in gram.

13. When a solute is dissolved in a solvent, the boiling point of the solvent

(i) remains unchanged (ii) increases (iii) decreases (iv) sometimes increases and sometimes decreases.

14. The elevation in boiling point is directly proportional to the concentration of solute in

(i) gm/ml (ii) moles/litre (iii) gm/litre (iv) volume/litre.

15. Which of the following has the highest boiling point ?

(i) N/10 urea (ii) N/10 glucose (iii) N/10 $NaCl$ (iv) N/10 $BaCl_2$.

16. When 1 mole of a solute is dissolved in 1000 gm of a solvent, the elevation in boiling point is called

(i) normal elevation point (ii) solution constant (iii) molal elevation constant (iv) cryoscopic constant.

17. The method used to determine the elevation in boiling point is

(i) Cottrel's method (ii) Hofmann's method (iii) Landsberger method (iv) Morse method.

18. When 6·0 gm urea is dissolved in 1000 gm of water, the elevation in boiling point of water is 0·52°C. K_b for 1000 gm water is equal to

(i) 0·52°C (ii) 5·2°C (iii) 52·0°C (iv) 10°C (v) 20°C.

19. The relationship between the molal elevation constant (K_b) and the latent heat of evaporation (L) is expressed as

(i) $K_b = \dfrac{0·02T^2}{L}$ (ii) $K_b = \dfrac{0·002T^2}{L}$

(iii) $K_b = \dfrac{0·02L}{T^2}$ (iv) $K_b = \dfrac{0·00L^2}{T}$.

20. The molal elevation constant for 100 gm of water is

(i) 1·8 (ii) 18·0 (iii) (1·5 (iv) 2·5 (v) 1·15.

21. Beckmann Thermometer is used to measure

(i) relative lowering of vapour pressure
(ii) temperature in °C

(iii) temperature in °F

(iv) difference of temperature in °C.

22. Depression in freezing point of a solvent is proportional to

(i) concentration of a solute in gm/litre

(ii) concentration of a solute in moles/litre

(iii) concentration of the solute in moles per 1000 gm

(v) none of the above.

23. Molal depression constant is

(i) same for all solvents

(ii) different for different solvents

(iii) none of the above.

24. When 1 mole of a non-volatile solute is dissolved in 1000 gm of a solvent, the depression in freezing point of the solvent is known as the

(i) ebullioscopic constant   (ii) normal depression constant

(iii) molal depression constant   (iv) solution constant.

25. K_f for 100 gm water is 18·6. K_f for 1000 gm water will be

(i) 1860   (ii) 18600   (iii) 186   (iv) 1·86.

26. Which of the following will have the largest depression in freezing point ?

(i) M/10 solution of urea   (ii) M/10 solution of KCl

(iii) M/10 solution of $BaCl_2$.

27. Which of the following will have the highest osmotic pressure ?

(i) N/10 glucose (ii) N/10 urea (iii) N/10 $NaCl$ (iv) N/10 fructose.

28. A solution A is found to have an osmotic pressure 2·5 atm, whereas another solution B has an osmotic pressure 3·6 atm. The solution A, with respect to B, is said to be

(i) isotonic (ii) hypotonic (iii) hypertonic.

29. M/10 solution of glucose is said to be hypertonic with respect to

(i) M/10 solution of urea   (ii) M/20 solution of urea

(iii) M/5 solution of urea.

30. The osmotic pressure of a solution is

(i) constitutive property   (ii) additive property

(iii) extensive property   (iv) colligative property.

Numerical Problems :

1. Freezing point of a biological fluid is −0·56°C. Calculate its osmotic pressure at 37°C assuming that change in the temperature does not change its solution characteristic. $K_f = 1·86$°C per 1000 gm of H_2O)   **(I. I. T. Pattern)**

[Solution : We know that,

$$\Delta T_f = K_f. \frac{w \times 1000}{m \times W}.$$

Here, $\Delta T_f = 0·56$°C, $K_f = 1·86$. If weight of water = 1 gm = W, then

$$0·56 = 1·86 \times \frac{w}{m} \times 1000$$

or $$\frac{w}{m} = \frac{0·56}{1·86 \times 1000} = 0·3013 \times 10^{-3} \text{ mole/gm}$$

∴ Molality of the solution = $0·3013 \times 10^{-3} \times 10^3 = 0·3013$

From osmotic pressure equation we have,

$$PV = \frac{w}{m} RT$$

or $\qquad P = \dfrac{w}{m} \cdot \dfrac{RT}{V} = 0.3013 \times \dfrac{0.082 \times 310}{1} = 7.66 \text{ atm}]$

2. Calculate the osmotic pressure of a 10% solution of glucose at 27°C. (Molecular weight of glucose=180.)   (Ans. 13·68 atm)

3. The osmotic pressure of a solution of urea at 10°C is 500 mm. If the solution is diluted ten times its original volume, what will be the osmotic pressure of the diluted solution at 15°C ?   (Ans. 50·92 atm)

4. Calculate the osmotic pressure of a decinormal solution of $NaCl$ at 27°C, assuming that the salt is 90% dissociated at this dilution.   (Ans. 4·68 atm.)

5. Calculate the osmotic pressure at 25°C of an aqueous solution containing 30 g of urea, 3.01×10^{22} molecules of sucrose, and 0·01 mole of a non-volatile solute whose molecular weight is 80 in 1800 ml of water.   (Ans. 7·6. atm.)

6. What is the osmotic pressure at 25°C in a solution containing 30 g of urea in 1800 ml of water ? Assuming no change in volume, what would be the osmotic pressure at 50° C ?   (Ans. 6·80 atm; 7·36 atm)

7. 17·32 g of a substance is dissolved in 100 ml of a solution. The osmotic pressure of this solution is the same as that of a solution of cane-sugar $(C_{12}H_{22}O_{11})$ containing 4·23 g of sugar in 100 ml of solution. Calculate the molecular weight of the substance.   (Ans. 140·1)

8. When 1·71 g of a substance is dissolved in 100 g of mercury, the vapour pressure of the latter decreases from 758 mm to 747·1 mm. If the molecular weight of mercury is 200, find the molecular weight of the solute.   (Ans. 237·8)

9. The vapour pressure of an aqueous solution of cane-sugar (molecular weight=342) is 756 mm. Calculate the amount of cane-sugar in 1000 g of water.   (Ans. 100·4 g)

10. The solution of non-electrolyte having molecular weight of 60 and containing 11 gm of the compound per litre was found to beisotonic with a decinormal sodium chloride. What is the apparent degree of ionisation of the electrolyte ?   (Ans. 83·33%)

11. A 0·10 molal solution of acetic acid in water freezes at 0·190°C. Calculate the per cent dissociation of acetic acid at this temperature.   (Ans. 2%)

12. The freezing point of pure camphor is 178·4°C and its molal freezing point constant is 40·0 m⁻¹. Find the freezing point of a solution containing 1·50 gm of a compound of molecular weight 125 in 25·0 gm of camphor.
(Ans. 13·7°C)

13. The boiling point of water is raised by 0·071°C when there is 1·7 gm of cane-sugar $(C_{12}H_{22}O_{11})$ in 25 gm of the solvent. Find out the molecular elevation of boiling point of water.   (Ans. 5·18°C)

14. The boiling point of ether is raised by 0·296°C on dissolving 1·19 gm of iodine in 35 gm of ether. Calculate the molecular weight of iodine. K_b for 100 gm of ether is 24·2.   (Ans. 255)

15. How many grams of urea must be added to 4000 gm of water to make the solution boil at 100·32°C ?   (Ans. 150·5 gm)

16. The aqueous solution of a certain non-volatile solute boils at 100·16°C at normal pressure. What is the molality ? What is its freezing point ? What is its vapour pressure at 100°C ?

17. A solution of $CaCl_2$ in water contains 4·8 gm per litre of it and boils at 100·057°C under atmosphere. Calculate the degree of ionisation of $CaCl_2$, if K_b for 100 gm of water is 5·2.   (Ans. 76·75%)

□ □ □

THE COLLOIDAL STATE

Crystalloids—Certain substances, such as sugars, salts, acids and bases can diffuse readily through a parchment paper. These substances are called "Crystalloids".

Colloids—Some substances, such as gelatin, albumen, glue and silicic acid diffuse through a parchment paper at a very slow rate. These are called "Colloids".

The colloidal state is a state of matter in which almost every substance can be brought by suitable means.

True solution—In a true solution, the particles of the solute exist as molecular dispersion in the solvent. These particles are so small that they find their place in the intermolecular space of the solvent.

Suspension—In this, the molecules of the substance remain suspended in the liquid. The suspended particles are visible through the naked eye or through a microscope. When the suspension is allowed to stand for some time, the particles of the substance settle down at the bottom of the vessel.

Examples : Dust particles in water, smoke in air, oil in water.

The dimensions of particles in suspension, colloid and true solutions are noted below.

System	Size of Particles
Suspension	bigger than 10^{-5} cm
Colloid	10^{-7}—10^{-5} cm
True solution	less than 10^{-7} cm

Types of Colloidal systems :

When finely divided particles of any substance with diameters lying between 10—$2000\overset{\circ}{A}$ is dispersed in any medium, the system so constituted is known as the **colloidal** system.

A colloidal system is a two-phased system, **dispersion medium and disperse phase.**

Dispersion Medium—This is a continuous medium in which the colloidal sized particles of the substance are dispersed.

Disperse Phase—The particles of the substance dispersed in the dispersion medium constitute the **disperse phase.**

Some examples of the colloidal system are given below—

Examples	Dispersion medium	Disperse phase
1. Fogs, Clouds	Gas	Liquid
2. Smoke	Gas	Solid
3. Foams	Liquid	Gas
4. Milk	Liquid	Liquid
5. Starch, Proteins	Liquid	Solid

Sols—The systems with solids as the disperse phase and a liquid as the dispersion medium are called **sols**.

Hydrosol—If the dispersion medium of the colloidal solution is water, the system is called **hydrosol**.

Aerosol—If the dispersion medium of the colloidal solution is air, the system is called 'aerosol.

Classification of Colloids

There are two types of colloids—

(i) Lyophilic and (ii) Lyophobic.

Lyophilic colloids—The substances, such as starch, proteins etc. which can pass readily into the colloidal state when mixed in a suitable solvent are known as the **lyophilic colloids**.

These colloids possess strong affinity (love) for the dispersion medium. They are much stable and are reversible.

Lyophobic colloids—The substances, such as As_2S_3, $Fe(OH)_3$, gold etc., which do not pass into the colloidal state easily are called **lyophobic colloids**.

These colloids are much less stable and irreversible.

Emulsion—An emulsion is a colloidal system in which the dispersion medium as well as the disperse phase are liquids.

Milk is an emulsion consisting of liquid fat as the disperse phase and water as the dispersion medium.

Gels—In a gel a liquid is dispersed in a solid.

Examples—Gelatin, agar agar etc.

Method of Preparation of Colloidal Solution

The colloidal solutions are generally prepared by the following two methods—

1. Dispersion Methods :

(A) Bredig's arc method—This process consists in producing an electric arc between wires of Pt, Au or Ag dipped in water.

At high temperature, the arc causes the metal to vaporize. The vapours are then condensed by water to form colloidal particles. A trace of $NaOH$ is added to stabilise the colloidal dispersion.

(B) Mechanical dispersion—This method consists in breaking the substance to the colloidal size. The solid substance and the dispersion medium are put between the surfaces of a grinding mill, rotating at high speed. The substance breaks down to the colloidal size particles.

(C) Peptization—The ionic solids containing a small amount of a common ion usually break down spontaneously into colloidal particles. This process is known as peptization.

A precipitate of AgI is peptized by shaking with a dilute solution of KI.

2. Condensation Methods :

(A) Reduction—The solution of the soluble salt is reduced by using suitable reducing agent (formaldehyde, hydrazine, H_2, CO etc.). For example, a colloidal solution of gold is prepared as follows :

A few drops of 0.1% $AuCl_3$ solution is added to 100 ml of water. $AuCl_3$ is neutralized by the requisite amount of K_2CO_3. A few drops of tannin (0.1%) is added and the solution warmed. Red gold sol is obtained.

(B) Oxidation—Colloidal sulphur is prepared by this method. H_2S gas is passed into an aqueous solution of SO_2.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$
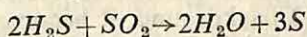
(C) Double decomposition—A colloidal solution of As_2S_3 is prepared by passing H_2S into an aqueous solution of As_2O_3.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$
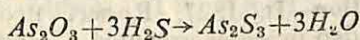
Excess of H_2S is removed by boiling the solution.

(D) Hydrolysis—The oxide and the hydroxide sols are prepared by this method.

When a solution of $FeCl_3$ is poured into a large volume of boiling water, a red colloidal solution of $Fe(OH)_3$ is produced.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$
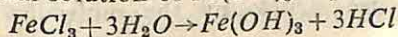
Purification of Colloidal Solution

The colloidal solution often contains impurities, like electrolytes. The presence of electrolytes in colloidal solution makes the sol unstable. So, the sol has to be purified. Usually the following two methods are used—

1. Dialysis—The colloidal solution is placed in a parchment bag. This is then kept in a wider vessel containing pure water. The electrolytes diffuse out into the water while the colloids are left behind in the bag. **"The process of purifying a colloidal solution from the electrolytes with the help of animal membranes, collodion or parchment is known as dialysis."**

The membrane used is called dialyser.

1. Electro-dialysis—Dialysis can be hastened by the application of an electric field, if the substance is an electrolyte. This is called **electro-dialysis.**

2. Ultrafiltration—The colloids can be separated from the solutes by passing the colloidal solution through a filter paper soaked in gelatin solution. This process is called **ultrafiltration.** Such a filter paper is called **ultra-filter.** The ultra-filters allow the passage of ions or molecules of the true solution but the pores of the ultra-filter are small enough to allow the passage of colloidal particles.

Properties of Colloidal Solutions :

1. Heterogeneous in character—A colloidal solution is heterogeneous. It consists of a disperse phase suspended in the dispersion medium.

2. Diffusibility—The colloidal particles cannot easily diffuse through animal membranes or parchment.

3. Filtrability—The colloidal particles can easily pass through an ordinary filter paper.

4. Tyndall effect—Whenever a beam of light is passed through a colloidal system, the particles of the disperse phase scatter the light in all directions. If the particle is viewed through a microscope against a dark background, it becomes visible as a speck of light. The scattering of light by colloidal particles is known as the **Tyndall** effect.

5. Brownian motion—In 1827, Robert Brown observed that pollen grains suspended in water executed a random zig-zag motion.

In fact, all colloidal particles execute this random zig-zag motion. This motion of colloidal particles is known as **Brownian motion.**

The Brownian motion is due to molecular motion. The small colloidal particles are struck by the molecules of the dispersion

medium from all sides.   This motion becomes less and less prominent as the size of colloidal particle grows.

6. Electrophoresis— When a hydrophobic sol is placed under the influence of an electric field, the particles are found to move in one direction only, i.e., towards a particular electrode. This phenomenon is known as electrophoresis.

The movement of colloidal particles towards the particular electrode gives us an idea about the nature of the electrical charge on the colloidal particles.

Coagulation of colloids : The coagulation or precipitation of a sol can be brought about by the addition of an electrolyte. The charge on the electrolyte neutralises the charge on the colloidal particles. In this connection, Hardy-Schulz law is important. According to this rule, "the precipitating power of an electrolyte depends upon the valency of the metal ion of the electrolyte".

Thus, the increasing order of precipitating power is—

$$Na^+ < Ba^{++} < Al^{+++}$$
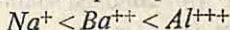
Protection of Colloids :

The lyophilic colloids are much more stable than lyophobic colloids because they are extensively solvated. The lyophilic colloids are covered by a thin layer of the solvent. This layer prevents them from aggregation.   That is why, lyophilic colloids have high viscosity.

Lyophilic colloids protect the lyophobic colloids from coagulation by the action of electrolytes. Such lyophilic colloids are called (protective colloids'. For example, if a little amount of gelatin 'lyophilic colloid) is added to a gold sol (lyophobic colloid), the latter is protected from coagulation. A much higher concentrtion of NaCl solution (electrolyte) will now be needed to cause precipitation or coagulation.

Gold number :

The lyophilic colloids differ in their protective powers. The protective powers are measured in terms of gold number.

The gold number is defined as the weight in milligram of the protective colloid which can just prevent the coagulation of 10 ml of a given gold sol. on the addition of 1 ml of a 10% solution of NaCl.

Questions

Long Answer Type :

1. What are colloids ?   How are they prepared and purified ?
2. What are lyophilic and lyophobic colloids ?
3. Write short notes on—
   (a) Gel   (b) Hardy-Schulz rule.   (c) Brownian motion   (d) Tyndall effect
(e) Electrophoresis   (f) Gold number

Short Answer type :

1. What is dialysis ?
2. Distinguish between a crystalloid and a colloid ?
3. Write short notes on—
   (i) Sol   (ii) Hydrosol   (iii) Aerosol.
4. What is diffe'ence between emulsion and gel ?
5. What are protective colloids ?

Objective Questions :

1. The size of the colloidal particle is
   (i) 10^{-7} to 10^{-5} cm   (ii) less than 10^{-7} cm
   (iii) greater than 10^{-5} cm   (iv) equal to 10^{-14} cm.
2. Which of the following does not diffuse through an animal membrane ?
   (i) $NaCl$ solution   (ii) Sugar   (iii) Starch.
3. Milk is
   (i) emulsion   (ii) gel   (iii) colloidal solution.
4. Colloidal particles are generally
   (i) positively charged   (ii) negatively charged (iii) positively or negatively charged.
5. Smoke is
   (i) an emulsion   (ii) a suspension   (iii) a colloid.

□ □ □

CATALYSIS

What is Catalysis ?

A catalyst is a substance which is capable of influencing the rate of a chemical reaction without itself undergoing any change in composition at the end of the reaction. Such a phenomenon is known as **Catalysis**.

In the reaction, $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$, MnO_2 is used as a catalyst.
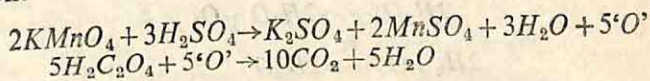
Types of Catalysts—

(i) **Positive catalyst**—The substance which can enhance the rate of a chemical reaction is known as the positive catalyst.

For example, MnO_2 used in the thermal decomposition of $KClO_3$ acts as a positive catalyst because it causes the decomposition of $KClO_3$ at a much lower temperature.

(ii) **Negative catalyst**—A catalyst which retards the rate of chemical reaction is known as the negative catalyst.

For example, a small amount of glycerine added to hydrogen peroxide slows down the decomposition of the latter. Hence, glycerine acts as a negative catalyst. Similarly, a small amount of ethyl alcohol appreciably decreases the oxidation of Na_2SO_3 to Na_2SO_4.

(iii) **Auto-catalyst**—In some reactions, one of the products of the reaction itself acts as a catalyst. Such a catalyst is called **auto-catalyst**. For example, in the oxidation of oxalic acid by acidified $KMnO_4$, $MnSO_4$ formed in the reaction increases the rate of oxidation.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5'O'$$
$$5H_2C_2O_4 + 5'O' \rightarrow 10CO_2 + 5H_2O$$

Promoters—A substance which promotes the activity of a catalyst is called a **promoter**. Molybdenum increases the activity of iron in the manufacture of NH_3 by Haber's process.

$$N_2 + 3H_2 \underset{(Mo)}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$
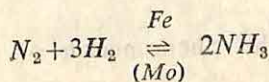
Mo is thus a promoter in this reaction.

Characteristics of Catalysis :

(i) A catalyst comes out unchanged in amount and chemical composition at the end of the reaction.

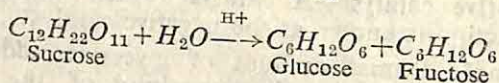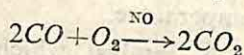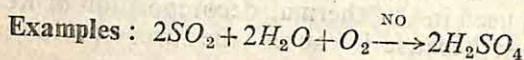(ii) Only a small amount of the catalyst is required to change the rate of reaction.

(iii) A catalyst does not change the position of equilibrium. It brings about the change in both the forward and the reverse reaction to the same extent.

(iv) A catalyst does not change the nature of products of the reaction.

(v) Catalytic poisons—Some substances inhibit or retard the rate of catalysed reactions. Such substances are called **catalytic poisons**. For example, in the presence of arsenic the rate of oxidation of SO_2 to SO_3 by O_2 is slowed down considerably. Thus, arsenic is a catalytic poison.

Homogeneous Catalysis :

When the catalyst and the reacting substances are in the same phase, the catalysis is called homogeneous catalysis.

Examples : $2SO_2 + 2H_2O + O_2 \xrightarrow{NO} 2H_2SO_4$

$$2CO + O_2 \xrightarrow{NO} 2CO_2$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$
$\underset{\text{Sucrose}}{}$

Heterogeneous catalysis :

In this catalysis the catalyst and the reacting substances are in different phases.

Examples :

$$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$
$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$
$$2SO_2 + O_2 \xrightarrow{Pt} 2SO_3.$$
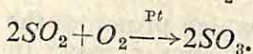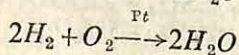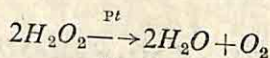
Theories of Catalysis :

In order to explain the phenomenon of catalysis, two theories have been proposed :

1. **Intermediate Compound Theory**—In this theory, it is postula-

ted that the catalyst combines with the reactants to form an inter-mediate compound. The latter is unstable and decomposes to form the product.

$$AB \quad + \quad S \quad \rightarrow \quad AS \quad + \quad B$$
(One reactant)   (Catalyst)   (Intermediate   (One product)
                                        compound)

$$AS \quad + \quad C \quad \rightarrow \quad AC \quad + \quad S$$
                (Second reactant)   (Second product)

Therefore, the overall reaction is,

$$AB + C \xrightarrow[\text{(catalyst)}]{S} AC + S$$

In the thermal decomposition of $KClO_3$ in presence of MnO_2 as catalyst, the reaction is believed to occur according to the following mechanism—
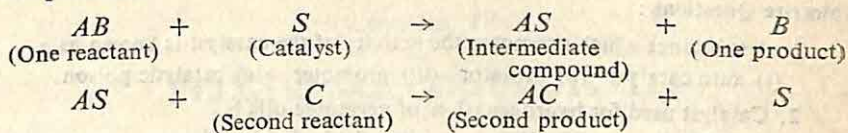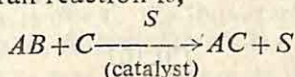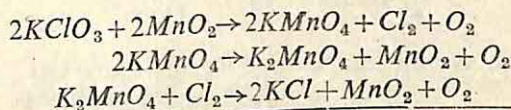
$$2KClO_3 + 2MnO_2 \rightarrow 2KMnO_4 + Cl_2 + O_2$$
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
$$\underline{K_2MnO_4 + Cl_2 \rightarrow 2KCl + MnO_2 + O_2}$$

Over all reaction : $2KClO_3 \xrightarrow[\text{catalyst}]{MnO_2} 2KCl + 3O_2$

2. The Adsorption Theory—According to this theory, the reactants are adsorbed on the surface of the catalyst to form a film. As the concentration of the reactants is high in the film, the reaction takes place at a much faster rate.

It has been shown that at the surface of the catalyst there are **active centres** where adsorption of the reactants occur.

Applications of Catalysts—

Process	Catalyst
(i) Manufacture of H_2SO_4 $\quad 2SO_2 + O_2 \rightarrow 2SO_3$ $\quad SO_3 + H_2O \rightarrow H_2SO_4$	V_2O_5
(ii) Synthesis of NH_3 $\quad N_2 + 3H_2 \rightleftharpoons 2NH_3$	Fe, Mo
(iii) Ostwald's process for HNO_3	Pt gauze
(iv) Hydrogenation of oils	Ni (finely divided)
(v) Deacon's process for the manufacture of Cl_2	Cu_2Cl_2

Questions

1. Define 'catalyst'.
2. Mention the role of a catalyst in a chemical reaction.

3. Explain 'homogeneous' and 'heterogeneous' catalysis with examples.
4. How is the effectiveness of a catalyst destroyed ?
5. What is adsorption theory of catalysis ?

Objective Questions :

1. A substance which promotes the activity of the catalyst is known as a
   (i) auto catalyst (ii) initiator (iii) promoter (iv) catalytic poison.

2. Catalyst used for hydrogenation of vegetable oils is
   (i) *Pt* black   (ii) Al_2O_3 (iii) finely divided nickel
   (iv) Anhydrous $AlCl_3$ (v) Copper metal.

□ □ □

ELECTRICAL CONDUCTIVITY

Electrolytes are also the conductors of electricity. The conductance of an electrolyte is due to the ions it contains. The conductance in aqueous solution follows Ohm's law.

"The resistance offered by a solution is directly proportional to the distance between the electrodes and inversely proportional to the area of the cross-section of the solution between the electrodes."

i.e.,
$$R \propto \frac{l}{A}, \qquad \text{or} \qquad R = \rho \, \frac{l}{A}$$

where, ρ = is the proportionality constant known as the specific resistance (resistivity).

When $l = 1$ cm and $A = 1$ cm^2, then
$$R = \rho.$$

Thus, the specific resistance is defined as the resistance of a solution enclosed between electrodes 1 cm apart and the area between the electrodes being 1 cm^2.

Conductance (L)—The reciprocal of resistance (R) is called conductance.

Thus,
$$L = \frac{1}{R}.$$

Conductance is expressed in ohm^{-1} or mho.

Specific conductance (κ)—The reciprocal of specific resistance (ρ) is called specific conductance. Thus,

$$\kappa = \frac{1}{\rho}, \qquad \text{or} \qquad \kappa = \frac{l}{A.R} = \left(\frac{l}{A}\right) \times \left(\frac{1}{R}\right).$$

$\therefore \quad \dfrac{l}{A} = x$ (cell constant) and $\dfrac{1}{R} =$ conductace,

$\therefore \quad \kappa = $ cell constant $\times$ conductance
or $\quad$ Specific conductance = Cell constant $\times$ Conductance.

$\therefore \quad$ Cell constant $= \dfrac{\text{Specific conductance}}{\text{Measured conductance}}.$

Unit of κ (Kappa)—
$$\kappa = \frac{l}{A} \times \frac{1}{R} = \frac{cm}{cm^2} \times ohm^{-1} = ohm^{-1} \, cm^{-1}.$$

Equivalent conductance (Λ) :

It is the conducting power of all the ions produced by one gram equivalent of an electrolyte in solution. It may be defined as the specific conductance multiplied by volume of the solution in ml containing one gram equivalent of the electrolyte. Thus,

$$\Lambda = \kappa \times V.$$

If $C =$ concentration of the solution in gram equivalent per litre, then,

$$V = \frac{1000}{C}, \qquad \therefore \quad \Lambda = \frac{1000 \ \kappa}{C}.$$

Unit of equivalent conductance—

$$\Lambda = \kappa \times V = \frac{1000 \ \kappa}{C}$$

$$= \frac{ohm^{-1} \ cm^{-1}}{equiv. \ cm^{-3}} = ohm^{-1} \ cm^2 \ equiv^{-1}.$$

Molar conductance (μ) :

It is defined as the specific conductance of a solution multiplied by the volume of the solution in ml containing one gram mole of electrolyte.

i.e.,

$$\mu = \kappa \times V$$

If C is the concentration in mole per litre, then, $V = \dfrac{1000}{C}$.

$$\therefore \quad \mu = \frac{1000 \times \kappa}{C}.$$

Units of μ—The units of the molar conductance are $ohm^{-1} \ cm^2 \ mole^{-1}$.

Variation of Equivalent conductance with dilution :

The equivalent conductance increases with increase in dilution of the solution. This is due to increase in the number of ions as the solution is progressively diluted.

However, increase in the number of ions is much less than increase in the volume of the solution Thus, the number of ions per ml decreases. Hence, the specific conductance decreases on dilution.

Degree of ionisation (α) :

The degree of ionisation of an electrolyte is represented by the following expression :

$$\alpha = \frac{\Lambda_v}{\Lambda_\infty}$$

where, Λ_v = equivalent conductance at a particular concentration,

Λ_∞ = equivalent conductance at infinite dilution.

Ion conductance :

It has been found that,

$$\Lambda_\infty = \lambda_c + \lambda_a$$

λ_c = ion conductance of the cation at infinite dilution,
λ_a = ion conductance of the anion at infinite dilution.

Ionic mobility :

Ion conductance is related to ionic mobility as,

$$\lambda_c = KU_c, \quad \lambda_a = KU_a.$$

U_c and U_a are the mobilities of the cation and anion respectively at infinite dilution. K is known as Faraday. Its value is known to be 96,500 coulomb.

$$\therefore \quad \lambda_c = 96500 \times U_c, \quad \text{or} \quad U_c = \frac{\lambda_c}{96500}$$

Similarly,

$$U_a = \frac{\lambda_a}{96500}.$$

Ion conductance is expressed in ohm^{-1} whereas ionic mobility in cm sec^{-1}.

Kohlrausch's Law :

The measurements of equivalent conductances at infinite dilution have shown that—

(i) The difference in conductances of any two cations is about the same, irrespective of the nature of the anions with which they are attached.

(ii) The equivalent conductances of any two anions is about the same, irrespective of the nature of cations with which they are attached.

These facts led **Kohlrausch** to enunciate a law known as **Kohlrausch's law.** This law is stated as,

"**The value of equivalent conductance at infinite dilution for any electrolyte is equal to the sum of the ion conductances of the two ions.**"

Thus,

$$\Lambda_\infty = \lambda_c + \lambda_a$$

Numericals (solved)

1. The specific conductance of a decinormal solution of KCl at 18°C is 0·0112 ohm^{-1} cm^{-1}. The resistance of a cell containing the solution at 18°C was found to be 55 ohm. What is the cell constant ?

Solution : Resistance = 55 ohm;
∴ Measured conductance = $\frac{1}{55}$ ohm^{-1}.
Specific conductance = 0·0112 ohm^{-1} cm^{-1};

∴ Cell constant = $\dfrac{0·0112}{1/55}$ = 0·0112 × 55 = 0·616.

2. The resistance of $\dfrac{N}{2}$ solution of an electrolyte in a cell was found to be 45 ohm. Calculate the equivalent conductance of the solution if the electrodes in the cell are 2·2 cm apart and have an area of 3·8 cm^2.

Solution :

Cell constant = $\dfrac{\text{Distance between the electrodes}}{\text{Area}}$ = $\dfrac{2·2}{3·8}$;

Resistance = 45 ohm,
∴ Measured conductance = $\frac{1}{45}$ ohm^{-1}.

∴ Specific conductance, $\kappa = \left(\dfrac{2·2}{3·8} \times \dfrac{1}{45} \right)$ ohm^{-1} cm^{-1}

$$= 0·01286 \text{ ohm}^{-1} \text{ cm}^{-1}.$$

Volume containing 1 gm equivalent of electrolyte = 2000 ml.
∴ Equivalent conductance = 0·01286 × 2000 = 25·72 ohm^{-1} cm^2.

3. The equivalent conductances of CH_3COONa, HCl and $NaCl$ at infinite dilution are 91·0, 426·16 and 126·45 ohm^{-1} cm^2 respectively at 25°C. Calculate the equivalent conductance at infinite dilution for acetic acid.

Solution :

Let equiv. conductance at infinite dilution for CH_3COONa, HCl,

$NaCl$ and CH_3COOH be Λ'_∞, $''\Lambda_\infty$, Λ'''_∞ and Λ^a_∞ respectively. Then,

$$\Lambda'_\infty = \lambda_{Na^+} + \lambda_{CH_3COO^-} = 91 \cdot 0 \qquad \cdot\cdot \quad (i)$$
$$\Lambda''_\infty = \lambda_{H^+} + \lambda_{Cl^-} = 426 \cdot 16 \qquad \cdot\cdot \quad (ii)$$
$$\Lambda'''_\infty = \lambda_{Na^+} + \lambda_{Cl^-} = 126 \cdot 45 \qquad \cdot\cdot \quad (iii)$$
$$\Lambda^a_\infty = \lambda_{H^+} + c_{H_3 COO^-} = ? \qquad \cdot\cdot \quad (iv)$$

Add (i) and (ii) and subtract (iii) from the adduct,

$$\lambda_{Na^+} + \lambda_{CH_3 COO^-} + \lambda_{H^+} + \lambda_{Cl^+} - \lambda_{Na+} - \lambda_{Cl^-}$$

$$= 91 \cdot 0 + 426 \cdot 16 - 126 \cdot 45$$

or $\qquad \lambda_{H^+} + \lambda_{CH_3 COO^-} = 390 \cdot 71$

or $\qquad \Lambda^a_\infty = 390 \cdot 71$ ohm^{-1} cm^2.

Questions

1. What is a cell constant ?

2. Distinguish between equivalent conductance and specific conductance.

3. Explain why specific conductance decreases while equivalent conductance increases on dilution ?

4. What do your understand by molar conduction ? Mention the unit in which it is expressed.

Objective Questions :

1. Conductivity of a solution is

(i) equal to its resistance, (ii) equal to its specific resistance. (iii) reciprocal of its resistance, (iv) three times its resistance.

2. As the solution of an electrolyte is diluted, the specific conductance of the solution

(i) increases (ii) decreases (iii) remains unchanged.

3. Equivalent conductance of an electrolyte solution

(i) increases on dilution (ii) decreases on dilution (iii) remains unchanged on dilution.

4. Equivalent conductance is represented by the expression

(i) $\dfrac{\kappa}{V}$ (ii) $\dfrac{\kappa}{R}$ (iii) $\kappa \times V$ (iv) $\kappa + V$.

5. Which of the following solutions will be more conducting ?

(i) Conc. H_2SO_4 (ii) N-H_2SO_4 (iii) $\dfrac{N}{10} H_2SO_4$.

Ans. 1. (iii); 2. (ii); 3. (i); 4. (iii); 5. (iii).

□ □ □

SOLUBILITY PRODUCT

In the saturated solution of the salt, there exists an equilibrium between the undissolved salt and the ions from the dissolved salt.

$$AB \rightleftharpoons A^+ + B^-$$
$$\text{(solid)} \quad \text{(in solution)}$$
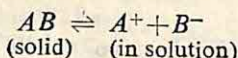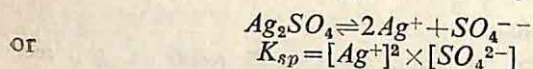
Applying the law of mass action,

$$K = \frac{[A^+] \times [B^-]}{[AB]}$$

where, K = equilibrium constant

or $\qquad [A^+] \times [B^-] = K[AB]$.

Since concentration of undissolved substance is taken to be constant, hence $K[AB] = K_{sp}$. K_{sp} is called the **solubility product** of AB.

The solubility product of Ag_2SO_4 will be given as

or
$$Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{--}$$
$$K_{sp} = [Ag^+]^2 \times [SO_4^{2-}]$$

Similarly, the solubility product for

$$A_mB_n \rightleftharpoons mA^+ + nB^-$$
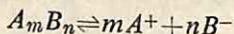
will be

$$K_{sp} = [A^+]^m \times [B^-]^n.$$

Thus, the solubility product of a solute may be defined as

"The solubility product of a salt forming a saturated solution in water is given by the product of the concentrations of ions raised to a power equal to the number of times the ions occur in the equation representing the dissociation of the electrolyte."

Relation between Solubility and Solubility Product :

The solubility product of $AgCl$ is given as

$$K_{sp} = [Ag^+] \times [Cl^-] \qquad \qquad \text{.. (i)}.$$

Solubility of $AgCl$ is expressed as

$$S = [Ag^+] = [Cl^-], \quad \therefore \quad K_{sp} = S \times S$$

or $\qquad S^2 = K_{sp}, \qquad \qquad$ or $\qquad S = \sqrt{K_{sp}}$.

Application of Solubility product principle :

1. Precipitations reactions—The precipitation of a sparingly soluble substance can be predicted with the help of solubility product principle.

A substance is precipitated when the product of concentrations of its ions in solution exceeds the value of the solubility product of the substance. Thus, $NaCl$ from the solution will get precipitated only when,

$$[Na^+] \times [Cl^- > K_{sp} \text{ for } NaCl].$$

2. Precipitation of Sulphides—In qualitative analysis, the metals of group II and IIIB get precipitated on the passage of H_2S.

Group II : The solution containing group II metal ions is made acidic by adding dil. HCl. H_2S is then passed. The sulphides of metals are precipitated.
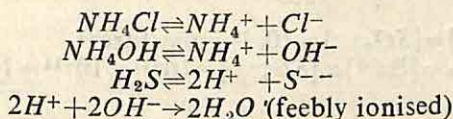
H_2S is a weak acid. It ionises as

$$H_2S \rightleftharpoons 2H^+ + S^{--}$$

In presence of H^+ ions from HCl, the ionisation of H_2S is suppressed. The concentration of S^{--} ions in solution, thus, becomes much smaller. Even then it is larger than that needed for the solubility products of the sulphides of Cu, Cd, Bi, Hg (ic), As, Sb and Sn to be exceeded. Hence, these cations get precipitated as sulphides.

Group III B : This group includes Ni, Co, Mn and Zn. The solubility products of sulphides of these metals are comparatively higher. In presence of H^+ ions (HCl) the S^{--} ion concentration is smaller than that required to cause their precipitation in group II.

So, in order to get an increased concentration of S^{--} ions the solution is made alkaline. For this, the solution is treated with solid NH_4Cl followed by addition of NH_4OH till the solution is alkaline. H_2S is now passed. Due to increase in the degree of ionisation of H_2S the S^{--} ion concentration in solution becomes higher.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$H_2S \rightleftharpoons 2H^+ + S^{--}$$
$$2H^+ + 2OH^- \rightarrow 2H_2O \text{ (feebly ionised)}$$

Due to consumption of H^+ ions in the last reaction more and more H_2S ionises. So, concentration of S^{--} ions in solution is increased appreciably. Thus, in solution, $[M^{++}] \times [S^{--}]$ exceeds the values of solubility product for MS (metal sulphide). As a result, these sulphides of metals get precipitated.

3. Precipitation of Hydroxides of group III A—Group III A contains Fe, Al and Cr. The solution containing these metal ions is treated with solid NH_4Cl. NH_4OH is then added in excess till the

solution smells strongly of NH_3.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \text{ (large ionisation)}$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
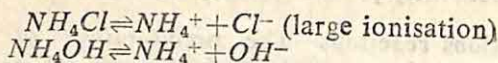
Due to the presence of common ions (NH_4^+) the dissociation of NH_4OH is suppressed. In solution, therefore, $[OH^-]$ becomes smaller. However, it is larger than that required to cause the precipitation of the hydroxides of Fe, Al and Cr, because the solubility product values of the latter are small.

Problems :

1. The solubility product of $Mg(OH)_2$ at 25°C is $1·4 \times 10^{-11}$. What is the solubility of $Mg(OH)_2$?

Solution—

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$
$$\therefore \quad K_{sp} = [Mg^{++}] \times [OH^-]^2$$
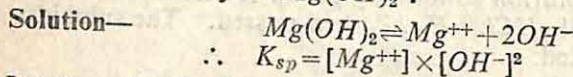
Let the solubility be s mole litre^{-1}.

$$\therefore \quad [Mg^{++}] = s$$
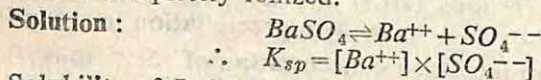
Since each Mg^{++} ion has two OH^- ions, hence

$$[OH^-] = 2s$$

$$\therefore \quad K_{sp} = s \times (2s)^2 = 4s^3, \quad \text{i.e.,} \quad 4s^3 = 1·4 \times 10^{-11}$$
or
$$s = 1·5 \times 10^{-4} \text{ mole litre}^{-1} = 58 \times 1·5 \times 10^{-4} \text{ g litre}^{-1}$$
$$= 0·0087 \text{ g litre}^{-1}.$$

2. The solubility of $BaSO_4$ is $2·33 \times 10^{-6}$ g per ml at 20°C. Calculate the solubility product of $BaSO_4$ assuming that the dissolved salt is completely ionized.

Solution :

$$BaSO_4 \rightleftharpoons Ba^{++} + SO_4^{--}$$
$$\therefore \quad K_{sp} = [Ba^{++}] \times [SO_4^{--}]$$

Solubility of $BaSO_4 = 2·33 \times 10^{-6}$ g per ml.

$$= 2·33 \times 10^{-9} \text{ g litre}^{-1}$$

$$= \frac{2·33}{233} \times 10^{-3} \text{ mole litre} = 10^{-11} \text{ mole litre}^{-1}.$$

Thus, $[Ba^{++}] = [SO_4^{--}] = 10^{-11}$ mole litre^{-1}.

$$\therefore \quad K_{sp} = [Ba^{++}] \times [SO_4^{--}] = 10^{-11} \times 10^{-11} = 10^{-22} \text{ mole litre}^{-1}.$$

Questions

1. Define 'solubility product' and on the basis of solubility product explain the following—

(i) NH_4Cl is added before adding NH_4OH solution to precipitate the hydroxides of the third group.

(ii) Before passing H_2S the filtrate from the first group is acidified with HCl.

(Roorkee Adm. Test 1982)

2. Derive the relationship between 'solubility' and 'solubility product'.

3. Explain the solubility product principle in the precipitation of the hydroxides of group IIIA metals in qualitative analysis.

Objective Questions :

1. A saturated solution of Ag_2SO_4 is $2 \cdot 5 \times 10^{-2}$M. Then, the value of its solubility product will be

    (i) $6 \cdot 25 \times 10^{-3}$ (ii) $6 \cdot 25 \times 10^{-5}$
    (iii) $1 \cdot 25 \times 10^{-3}$ (iv) $1 \cdot 25 \times 10^{-5}$.

2. Ammonium chloride is added in the third group to

    (i) catalyse the precipitation of the hydroxide of iron and aluminium.
    (ii) prevent the precipitation of the hydroxide of the fourth group cations and Mg.
    (iii) prevent the formation of the hydroxide of group IV cations.
    (iv) convert Fe^{++} to Fe^{+++} ions.

□ □ □

HYDROLYSIS OF SALTS

Hydrolysis—The interaction between the ion (or ions) of a salt and the ions of water is called **hydrolysis**.

When a salt is dissolved in water, the solution is not always neutral in reaction. Interaction may occur with the ions of water. The resulting solution will be neutral, acid or alkaline according to the nature of the salt.
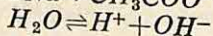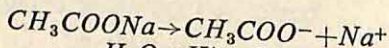
Salts may be divided into four main classes—

1. Salts of strong acids and strong bases, i.e. $NaCl$, KCl etc.
2. Salts of weak acids and strong bases, i.e., CH_3COONa.
3. Salts of strong acids and weak bases, i.e., NH_4Cl.
4. Salts of weak acids and weak bases, i.e., $HCOONH_4$, $(CH_3COO)_3\,Al$.

Salts of strong acids and strong bases—When such a salt $(NaCl)$ is dissolved in water, neither the anions (Cl^-) have any tendency to react with H^+ ions nor the cations (Na^+) with the OH^- ions of water. Since the parent acid (HCl) and base $(NaOH)$ are strong electrolytes, the equilibrium between the H^+ and OH^- ions in water,

$$H_2O \rightleftharpoons H^+ + OH^-$$
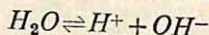
is not disturbed. Hence, the solution remains neutral.

Salts of weak acids and strong bases—A salt of this class is CH_3COONa. When this is dissolved in water, the following equilibria exist in solution :

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

CH_3COO^- reacts with the H^+ ion and Na^+ with the OH^- ion.

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH \text{ (feebly ionized)}$$
$$Na^+ + OH^- \rightarrow NaOH \quad \text{(completely ionized)}$$
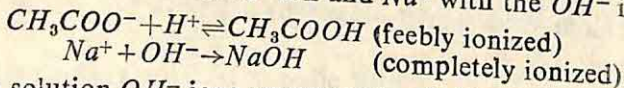
Thus, in solution OH^- ions concentration is highly increased as compared to H^+ ions. **The solution, therefore, becomes alkaline.**

Salts of strong acids and weak bases—NH_4Cl is a salt of this class. In an aqueous solution of NH_4Cl the following equilibria exist :

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \text{ (feebly ionized)}$$
$$H^+ + Cl^- \rightarrow HCl \quad \text{(completely ionized)}$$
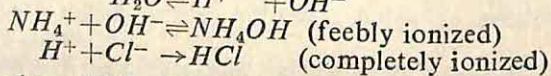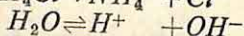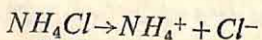
Thus, in solution $[H^+] > [OH^-]$. Hence, the solution becomes acidic.

Salts of weak acids and weak bases—In an aqueous solution of such a salt, two reactions occur simultaneously.

$$M^+ + H_2O \rightleftharpoons MOH + H^+ \qquad \text{.. (i)}$$
$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad \text{.. (ii)}$$
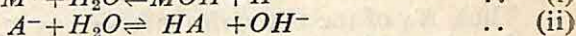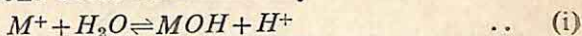
The reaction of the solution depends on the relative dissociation constants of the acid (K_A) and the base (K_B).

When $K_A = K_B$, the solution is neutral.
When $K_B > K_A$, the solution is alkaline.
When $K_A > K_B$, the solution is acidic.

Hydrolysis constant—Let us consider the hydrolytic reaction of CH_3COONa.

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$
$$\text{or} \qquad CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
$$\underset{\substack{\text{(Unhydrolysed} \\ \text{salt)}}}{} \qquad \underset{\text{(Free acid)}}{} \quad \underset{\text{(Free base)}}{}$$
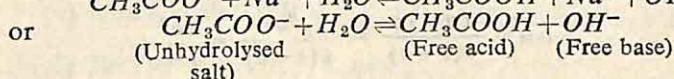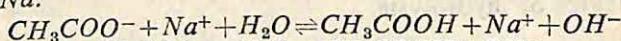
Applying the law of mass action,

$$K = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-] \times [H_2O]}$$

or
$$K[H_2O] = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-]}.$$

Since the concentration of H_2O is constant,

hence,
$$K_H = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-]}.$$

K_H is a constant known as the hydrolysis 'constant.

Relation between K_H, K_A and K_W—In the hydrolysis of CH_3COONa the following equilibria exist in solution—

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad \text{.. (i)}$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad \text{.. (ii)}$$
$$H_2O \rightleftharpoons H^+ + OH^- \qquad \text{.. (iii)}$$
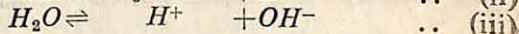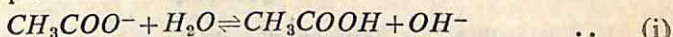
From equation (i) :
$$K_H = \frac{[CH_3COOH] \times [OH^-]}{[CH_3COO^-]}$$

From equation (ii) :
$$K_A = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

From equation (iii) :
$$K_W = [H^+] \times [OH^-].$$

Now
$$\frac{K_W}{K_A} = \frac{[CH_3COOH] \times [OH^+]}{[CH_3COO^-]} = K_H$$

or
$$K_H = \frac{K_W}{K_A}.$$

Thus, K_H of the salt varies inversely as K_A of the weak acid, i.e., weaker the acid greater is the hydrolysis constant of the salt.

Degree of hydrolysis—The degree of hydrolysis of a salt is defined as the fraction of the total salt that is hydrolysed at equilibrium stage.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
$$c(1-\alpha) \qquad\qquad ca \qquad\quad ca$$
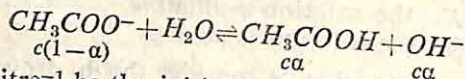
Let c mole litre^{-1} be the initial concentration of sodium acetate. α is the degree of hydrolysis.

$$\therefore \quad K_H = \frac{ca \times ca}{c(1-\alpha)} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{ca^2}{1-\alpha}.$$

When α is small compared to unity, then
$$K_H = c\alpha^2$$

$$\therefore \quad \alpha = \sqrt{\frac{K_H}{c}}.$$

But
$$K_H = \frac{K_W}{K_A}, \qquad \therefore \quad \alpha = \sqrt{\frac{K_W}{K_A.c}}.$$

Thus, (a) smaller the value of K_A greater is the value of α.
(b) As K_W increases with temperature and K_A changes only slightly, α increases rapidly with rise in temperature.
(c) α increases when c decrease.

Questions

1. What is meant by 'hydrolysis of salts' ?
2. Define the term 'degree of hydrolysis' and 'hydrolysis constant'.

□□□

CHAPTER 22

MISCELLANEOUS QUESTIONS WITH ANSWERS

1. Fill in the blanks and balance the equations—

    (i) $I_2 + Na_2S_2O_3 \rightarrow \ldots + NaI$

    (ii) $2Al + NaOH + \ldots \rightarrow \ldots + H_2$

    (iii) $KCl + MnO_2 + H_2SO_4 \rightarrow KHSO_4 + MnSO_4 + H_2O + \ldots$

    (iv) $H_2O_2 + I^- + H^+ \rightarrow 2H_2O + \ldots$

    (v) $NaIO_3 + NaHSO_3 \rightarrow \ldots + Na_2SO_4 + NaHSO_4 + H_2O$

<div align="right">(B. I. T. 1978)</div>

    (vi) $FeCl_3 + H_2S \rightarrow \ldots + HCl + \ldots$

    (vii) $FeS_2 + O_2 \xrightarrow{heat} \ldots + \ldots$

    (viii) $FeSO_4 + H_2SO_4 + 2HNO_3 \rightarrow \ldots + \ldots + \ldots$ (B. I. T. 1981)

Ans. (i) $I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

    (ii) $2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + H_2$

    (iii) $2KCl + MnO_2 + 3H_2SO_4 \rightarrow 2KHSO_4 + MnSO_4 + 2H_2O + Cl_2$

    (iv) $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$

    (v) $6NaIO_3 + 15NaHSO_3 \rightarrow 3I_2 + 6Na_2SO_4 + 9NaHSO_4 + 3H_2O$

    (vi) $2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S$

    (vii) $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

    (viii) $6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$.

2. Complete and balance the following equations—

    (i) $Zn + NO_3^- \rightarrow Zn^{++} + NH_4^+$

    (ii) $Cr_2O_7^{--} + C_2H_4O \rightarrow C_2H_4O_2 + Cr^{+++}$

    (iii) $HNO_3 + HCl \rightarrow NO + Cl_2$

    (iv) $Ce^{+++} + S_2O_3^{--} \rightarrow SO_4^{--} + Ce^{4+}$

    (v) $Cl_2 + OH^- \rightarrow Cl^- + ClO$.   (I. I. T. 1983)

Ans. (i) $4Zn + NO_3^- + 10H^+ \rightarrow 4Zn^{++} + NH_4^+ + 3H_2O$

    (ii) $Cr_2O_7^{--} + 3C_2H_4O + 8H^+ \rightarrow 3C_2H_4O_2 + 2Cr^{+++} + 4H_2O$

    (iii) $2HNO_3 + 6HCl \rightarrow 2NO + 3Cl_2 + 4H_2O$

    (iv) $2Ce^{3+} + S_2O_8^{--} \rightarrow 2Ce^{4+} + 2SO_4^{--}$

    (v) $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$.

3. Arrange the following according to the instructions given—

    (i) CO_2, CH_4, C_2H_5OH (in the increasing order of solubility in water).

    (ii) PbO, ZnO, MgO (in the increasing order of basic nature).

    (iii) Na, Cu, Zn (in increasing order of electro-positivity).

    (iv) Graphite, diamond, copper (in increasing order of electrical conductivity).

    (v) H_2, Cl_2, CH_4 (in increasing order of diffusion rate).

<div align="right">(B. I. T. 1979)</div>

Ans. (i) CH_4, CO_2, C_2H_5OH.
  (ii) PbO, ZnO, MgO.
  (iii) Cu, Zn, Na.
  (iv) Diamond, graphite, copper.
  (v) Cl_2, CH_4, H_2.

4. Match the following :

A. Isomers   (i) Graphite and Diamond
B. Isotopes   (ii) Ethanol and Dimethyl ether
C. Isomorphous   (iii) Na^+ and Mg^{++}
D. Allotropes   (iv) $FeSO_4.7H_2O$ & $MgSO_4.7H_2O$
E. Isobars   (v) $_8O^{14}$ and $_8O^{18}$
F. Isoelectronic   (vi) $_{20}Ca^{40}$ & $_{19}K^{40}$.

  Ans. A—(ii)
          B—(v)
          C—(iv)
          D—(i)
          E—(vi)
          F—(iii).

5. Name the scientific terms for the following :
  (i) A substance which promotes a chemical reaction without any change to itself.
  (ii) A reaction in which heat is absorbed.
  (iii) The gas used for making soda water.
  (iv) Inner core of the atom.
  (v) The pure form of a substance which cannot be decomposed by ordinary means.
  (vi) Property of a metal being drawn into wire.
  (vii) A substance which absorbs moisture from the air.
  (viii) A chemical reaction brought about by light.
  (ix) Reaction in which an acid and a base react.
  (x) A metal which exists in the form of liquid.
  (xi) Liquid used to wash negative in photography.
  (xii) Chemicals used for the growth of plants.

  Ans. (i) Catalyst,   (ii) Endothermic,   (iii) Carbon dioxide, (iv) Nucleus,   (v) Na_2CO_3,   (vi) Ductility,   (vii) Hygroscopic, (viii) Photochemical, (ix) Neutralization, (x) Mercury, (xi) Hypo, (xii) Fertilisers.

6. How can protons bonded in the nucleus be present with a repulsive force in such a small volume of nucleus ?

  Ans. Protons are held together in the nucleus by nuclear forces. A proton in the nuclear range $(1 \times 10^{-12}$ cm) experiences 40 times more attraction than the repulsive force. Nuclear forces are short range forces only.

7. How would you determine the valency of an atom ?

  Ans. The valency of an atom may be defined as the number of unpaired electrons exchanged during the formation of a bond.

In electrovalency the exchange is 100%, as in $NaCl$.

$Na : 1s^2 2s^2 2p^6 3s^1$ $Cl : 1s^2 2s^2 2p^6 3s^2 3p^5$
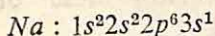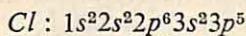
$\therefore$ Valency of $Na = 1$ Valency of $Cl = 1$

In covalency, sharing electrons occurs. BCl_3 is a covalent compound. In the normal state B has only one unpaired state, but in excited state it has 3. Hence, in BCl_3, valency of $B = 3$.

8. Explain why $AlCl_3$ is covalent in anhydrous state while hydrated $AlCl_3$ is electrovalent.   (I.I.T. Pattern)

Ans. $AlCl_3$ is largely a covalent compound. In order to form an electrovalent bond Al atom must lose three electrons to form Al^{+++}. For this 5122·4 kJ mole^{-1} of energy is needed. But when chemical reaction occurs only 1470 kJ mole^{-1} of energy is available. Hence, Al does not form electrovalent compound.

Hydrated $AlCl_3$ contains $[Al(H_2O_6]^{3+}$ ion. The hydration of $AlCl_3$ is an exothermic reaction. The energy released causes the transfer of three electrons from Al to three Cl atoms. Thus, hydrated $AlCl_3$ is an electrovalent compound.

9. Do gas-gas mixture form colloidal solutions ?

Ans. The gas-gas mixture cannot form colloidal solution, because the gases have tendency to diffuse into one another and form a homogeneous mixture.

10. What is an emulsion ? What are the different types of emulsions ? Give two tests which can be used to detect the type of an emulsion.

Ans. An emulsion is a colloidal system in which the dispersion medium as well as the disperse phase are liquids.

There are two types of emulsions—

(i) Oil in water emulsion and (ii) Water in oil emulsion.

Two tests—(a) Dry test—An oil soluble dye is shaken with the emulsion. A drop of it is then examined under a microscope. If the drop is coloured, the emulsion is of oil in water type.

(b) Spreading test—A drop of the emulsion is placed on the surface of oil. In case the drop spreads easily, the emulsion is water in oil type.

11. "In nuclear reactions, there is loss of an α-particle and the atom is expected to become negatively charged. Similarly, loss of a β-particle from the nucleus, the atom should become positively charged." Comment upon this situation.

Ans. The electrical neutrality of the newly formed atom is always maintained. The loss of an α-particle from the nucleus is accompanied by the loss of two planetary electrons to the surroundings so that the atom may remain electrically neutral. Similarly, the loss of a β-particle from the nucleus involves the gain of planetary electrons from the surroundings to keep the atom electrically neutral.

12. What is the nature of the nuclear forces ? How these differ from the electrostatic forces ?

Ans. There are attractive forces between proton and neutron, neutron and neutron and even between proton and proton. These forces are stronger than the repulsive forces due to positive charges on the protons. These attractive forces are called the **nuclear forces.**

The nuclear forces differ from the electrostatic forces in the respect that the former operate within small distances of approximately 10^{-15} m, whereas the latter operate over long ranges also. At distances greater than 1.4×10^{-12} m the nuclear forces drop to zero. So, nuclear forces are **short range forces** only.

Numerical Problems (solved)

1. A crystallised salt on being rendered anhydrous loses 45·6% of its water. The percentage composition of anhydrous salt is :
$Al = 10.5\%$, $K = 15.1\%$, $S = 24.8\%$ and $O = 49.6\%$. Calculate the simplest formula of the anhydrous and the formula of the crystallised salt.

Solution :

Element	Percentage	At. wt.	$\dfrac{Percentage}{At.\,wt.}$	Division by the least number	Simplest ratio
Al	10·5	27	$\dfrac{10.5}{27} = 0.39$	$\dfrac{0.39}{0.39} = 1$	1
K	15·1	39	$\dfrac{15.1}{39} = 0.39$	$\dfrac{0.39}{0.39} = 1$	1
S	24·8	32	$\dfrac{24.8}{32} = 0.78$	$\dfrac{0.78}{0.39} = 2$	2
O	49·6	16	$\dfrac{49.6}{16} = 3.10$	$\dfrac{3.10}{0.39} = 7.9$	8

$\therefore$ Simple formula is, $KAlS_2O_8$
Simple formula wt. $= 258$.

$\therefore$ 100 g of the salt in 45·6 g water,
$\therefore$ wt. of anhydrous salt in 100 g $= 100 - 45.6 = 54.4$ g.
Now, $\because$ 54·4 g salt combines with 45·6 g H_2O,

$\therefore$ 258 g salt combines with $\dfrac{45.6 \times 258}{54.4}$ g H_2O

$= 216$ g $H_2O = \frac{216}{18}$ mol of $H_2O = 12$
$\therefore$ Formula of the hydrated salt is, $KAlS_2O_8.12H_2O$.

2. 33·6 c. c. of phosphorus weigh 0·0625 g at 546°C and 76 cm pressure. What is the molecular weight of phosphorus ? How many atoms are there is one molecule of phosphorus vapour ?

(I. I. T. 1969)

Solution : Calculation of volume of vapour at N. T. P.—

$$P_1 = 760 \text{ mm}, \qquad P_2 = 76 \text{ cm} = 760 \text{ mm}$$
$$V_1 = 33\cdot6 \text{ c.c.}, \qquad V_2 = ?$$
$$T_1 = 273 + 546 \qquad T_2 = 273 \text{ K}$$
$$\quad = 819 \text{ K}.$$

$$\therefore \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}, \qquad \therefore \quad \frac{760 \times 33\cdot6}{819} = \frac{760 \times V_2}{273}$$

or $\quad V_2 = \dfrac{760 \times 33\cdot6 \times 273}{760 \times 819} = \dfrac{33\cdot6 \times 273}{819} \text{ c.c.}$

$$= 11\cdot2 \text{ c.c.}$$

$\therefore \quad 11\cdot2$ c.c. phosphorus vapour weighs $0\cdot0625$ g;

$\therefore \quad 22,400$ c.c. phosphorus vapour weighs $\dfrac{0\cdot0625 \times 22400}{11\cdot2}$ g.

$$= 125 \text{ g.}$$

Hence, mole. wt. of phosphorus $= 125$.

$\therefore \quad$ Atomic weight of phosphorus $= 31$,

$\therefore \quad$ No. of atoms in one molecule $= \frac{125}{31} = 4$.

3. To a sample of an element X (at. wt. $= 70$) another element Y (at. wt. $= 120$) is to be added as an impurity. The ratio of the atoms in the mixture is to be $1 : 10^{-7}$. How many grams of Y will be required for 35 grams of X ?

(I. I. T. Pattern).

Solution : Let the grams of Y in 35 grams of X be x.

Number of atoms in 35 g of X

$$= \tfrac{35}{70} N \qquad (N = \text{Avogadro's number}).$$
$$= \frac{N}{2}$$

Number of atoms in x g of $Y = \dfrac{x}{120} N$.

$$\therefore \quad \frac{N/2}{\frac{xN}{120}} = \frac{1}{10^{-7}}, \qquad \text{or} \qquad \frac{N}{2} \times \frac{120}{xN} = \frac{1}{10^{-7}}$$

or $\quad \dfrac{60}{x} = \dfrac{1}{10^{-7}}, \qquad$ or $\qquad x = 60 \times 10^{-7} = 6 \times 10^{-6}$ gram.

4. $0\cdot32$ g sulphur dioxide, $0\cdot42$ g carbon monoxide and $0\cdot22$ g nitrous oxide are contained in 250 ml vessel at 27°C. Calculate— (i) total pressure of the mixture, (ii) total molecules in the vessel, (iii) pressure of the mixture if the temperature is reduced to 10°.

Solution : Mole of $SO_2 = \dfrac{0.32}{64} = 0.005$

Mole of $CO = \dfrac{0.42}{28} = 0.015$

Mole of $N_2O = \dfrac{0.22}{44} = 0.005$

Total number of moles $= 0.005 + 0.015 + 0.005 = 0.025.$

(i) Total pressure :

$$PV = nRT, \qquad \text{or} \qquad P = \dfrac{nRT}{V} = \dfrac{0.025 \times 0.0821 \times 300}{1/4}$$

$$= 2.463 \text{ atm.}$$

(ii) Total molecules = Number of moles $\times 6.023 \times 10^{23}$
$$= 0.025 \times 6.023 \times 10^{23} = 1.5 \times 10^{22}.$$

(iii) Pressure of the mixture at 10°C.

$$\dfrac{P_1}{P_2} = \dfrac{T_1}{T_2}, \qquad \text{or} \qquad \dfrac{2.463}{P_2} = \dfrac{300}{283}$$

or $\qquad P_2 = \dfrac{2.463 \times 283}{300} = 2.323 \text{ atm.}$

5. 90 ml of O_2 and 50 ml of H_2 both measured at N. T. P. are mixed and allowed to expand to a total volume of 240 ml at 0°C. What is the total pressure of the mixture of gases ? What are the partial pressures of O_2 and H_2 respectively.

Solution : Total volume of mixture $= 90 + 50 = 140$ ml.

When the gas mixture is allowed to expand to volume 240 ml, let the pressure be P_2. Then,

$$\dfrac{760 \times 140}{273} = \dfrac{P_2 \times 240}{273}$$

or $\qquad P_2 = \dfrac{760 \times 140 \times 273}{240 \times 273} = 443.33 \text{ mm.}$

Partial pressure of H_2 :

$$50 \times 760 = p_{H_2} \times 240$$

$$\therefore \quad p_{H_2} = \dfrac{50 \times 760}{240} = 285 \text{ mm}$$

Partial pressure of O_2 :

$$90 \times 760 = p_{O_2} \times 240$$

or $$p_{O_2} = \frac{90 \times 760}{240} = 158 \cdot 33 \text{ mm.}$$

6. A pure gas has a density of $1 \cdot 50$ mg/ml at 303 K and 720 mm of Hg. Assuming ideal behaviour, calculate its molecular mass.

What is the number of (i) moles, (ii) molecules in one ml of gas at 303 K and 720 mm of pressure ?

Solution : $\because \quad \dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}, \qquad \therefore \quad \dfrac{720 \times 1}{303} = \dfrac{760 \times V_2}{273}$

or $$V_2 = \frac{720 \times 273}{760 \times 303} = 0 \cdot 8537 \text{ ml.}$$

$\because \quad 0 \cdot 8537$ ml of gas $= 1 \cdot 50 \times 10^{-3}$ g,

$\therefore \quad 22400$ ml of gas $= \dfrac{1 \cdot 50 \times 10^{-3} \times 22400}{0 \cdot 8537} = 39 \cdot 36$ g

i.e., molecular wt. $= 39 \cdot 36$.

(i) Mole of gas $= \dfrac{1 \cdot 50 \times 10^{-3}}{39 \cdot 36} = 3 \cdot 81 \times 10^{-5}$.

(ii) Number of molecules $= 3 \cdot 81 \times 10^{-5} \times 6 \cdot 023 \times 10^{23}$
$$= 2 \cdot 295 \times 10^{-19}.$$

7. The density of mercury is $13 \cdot 6$ g/ml. Calculate approximately the diameter of an atom of mercury assuming that each atom is occupying a cube of edge length equal to the diameter of the Hg atom. (I. I. T. 1983)

Solution : At. wt. of $Hg = 200$

Avogadro's number $= 6 \cdot 023 \times 10^{23}$
Number of atom in 1 g $Hg = \frac{1}{200} \times 6 \cdot 023 \times 10^{23} = 3 \cdot 012 \times 10^{21}$
Density of $Hg = 13 \cdot 6$ g/ml

$\therefore$ Volume of one atom $= \dfrac{1}{3 \cdot 012 \times 10^{21} \times 13 \cdot 6}$ ml $= 2 \cdot 45 \times 10^{-23}$ ml.

By the question, diameter of the Hg atom is equal to the edge length of the cube.

$\therefore$ Edge length or diameter $= (\text{volume})^{1/3}$

$$= (2 \cdot 45 \times 10^{-23})^{1/3} = 2 \cdot 905 \times 10^{-8} \text{ cm} = 2 \cdot 91 \text{ Å.}$$

8. Oxygen is present in a 1 litre flask at a pressure of $7 \cdot 6 \times 10^{-10}$ mm of Hg. Calculate the number of oxygen molecules in the flask at 0°C. (I. I. T. 1983)

Solution : Volume of oxygen = 1 litre

Pressure of gas = $7 \cdot 6 \times 10^{-10}$ mm of Hg

$$= \frac{7 \cdot 6 \times 10^{-10}}{760} \text{ atm} = 10^{-12} \text{ atm.}$$

Temp., $T = 273$ K

$R = 0 \cdot 082$ lit-atm K^{-1} mole^{-1}

$\therefore$ $PV = nRT$

or $10^{-12} \times 1 = n \times 0 \cdot 082 \times 273$

or $n = \dfrac{10^{-12}}{0 \cdot 082 \times 273} =$ Number of moles.

$\therefore$ Number of molecules $= \dfrac{10^{-12}}{0 \cdot 082 \times 273} \times 6 \cdot 023 \times 10^{23}$

$$= 2 \cdot 69 \times 10^{10}.$$

9. When 2 g of a gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atm. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1·5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$.

(I. I. T. 1983)

Solution : Increase in pressure when B is added

$$= 1 \cdot 5 - 1 = 0 \cdot 5 \text{ atm.}$$

We know that the pressure of a gas is directly proportional to the number of moles, provided T and V are constants.

$\therefore$ Number of moles in 2 g of gas A at 1 atm. pressure

$= \frac{1}{2} \times$ Number of moles in 3 g of B at 0·5 atm.

$=$ Number of moles in 6 g of B at 1 atm.

$\therefore$ $\dfrac{2}{M_A} = \dfrac{6}{M_B}$,   or $\dfrac{M_A}{M_B} = \dfrac{2}{6} = \dfrac{1}{3}$, i.e., $M_A : M_B = 1 : 3$.

10. 360 ml of a gas 'A' diffuse through a porous vessel in 30 minutes. 120 ml of SO_2 require 20 minutes to diffuse through the same vessel under identical conditions. The molecular weight of SO_2 is 64. Calculate the molecular weight of 'A'.

Solution : Rate of diffusion of gas 'A' $(r_1) = \frac{360}{30} = 12$

Rate of diffusion of SO_2 $(r_2) = \frac{120}{20} = 6$

Molecular weight of $A = x$

Molecular weight of $SO_2 = 64$.

From Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{64}{x}}, \qquad \text{or,} \qquad \frac{12}{6} = \sqrt{\frac{64}{x}}$$

or $2 = \sqrt{\dfrac{64}{x}}$,   or $4 = \dfrac{64}{x}$

$$\therefore \quad x = \tfrac{64}{4} = 16.$$

11. Calculate the relative rates of diffusion of $^{235}UF_6$ and $^{238}UF_6$ in the gaseous form.

Solution :

$$\frac{\text{Rate of diffusion of } ^{235}UF_6}{\text{Rate of diffusion of } ^{238}UF_6} = \sqrt{\frac{256 \cdot 996}{253 \cdot 996}} = \frac{1 \cdot 006}{1}.$$

12. An aqueous solution of sodium chloride contains $8 \cdot 00$ g of the salt per 100 g of solution at 25°C. Calculate the concentration of this solution on molal scale. (Mole wt. of $NaCl = 58 \cdot 5$)

Solution : Wt. of solvent $= 100 - 8 = 92$ g.

$$\text{Mole of } NaCl = \frac{8}{58 \cdot 5} = 0 \cdot 136$$

$$\therefore \quad \text{Conc. on molal scale} = \frac{0 \cdot 136 \times 1000}{92} = 1 \cdot 478.$$

13. What weight of urea should be added to 200 ml of water to get a $0 \cdot 1$ Molar solution ? (Mole. wt. of urea $= 60$).

Solution : $0 \cdot 1$ Molar solution means that 1000 ml of solution contains $0 \cdot 1$ mole urea.

Hence, 200 ml solution will contain $\dfrac{0 \cdot 1 \times 200}{1000}$ mole,

i.e., $\tfrac{1}{50}$ mole $= \tfrac{1}{50} \times 60 = 1 \cdot 2$ g urea.

14. What is the molarity of water in pure water ? (Sp. gr. $= 1$)

Solution : Sp. gr. of water $= 1$

$\therefore$ 1000 ml $= 1000$ g water

1000 g water $= \tfrac{1000}{18}$ mole $= 55 \cdot 55$ mole.

$\because$ 1000 ml water contains $55 \cdot 55$ mole H_2O,

$\therefore$ Molarity $= 55 \cdot 55$.

15. What is the molality and molarity of a solution of H_2SO_4 (sp. gr. $1 \cdot 2$) containing 72 g/litre of H_2SO_4 ?

Solution : Volume of $H_2SO_4 = \dfrac{72}{1 \cdot 2} = 60$ ml.

$\because$ 1000 ml of solution contains 60 ml H_2SO_4,

$\therefore$ 100 ml of solution contains $\dfrac{60 \times 100}{1000}$ ml $H_2SO_4 = 6\%$.

i.e., $\%$ strength $= 6$.

INTER. CH.-23

$\because$ 100 ml of the solution contains 6 ml of H_2SO_4,

$\therefore$ 1000 ml of the solution contains 60 ml of H_2SO_4

$\therefore$ Wt. of $H_2SO_4 = 60 \times 1.2 = 72$ g.

$\because$ Eq. wt. of $H_2SO_4 = 49$,

$$\therefore \quad \text{Normality} = \frac{72 \times 1000}{49} = 1.46 \ (N)$$

$$\therefore \quad \text{Molarity} = \frac{1.46}{2} = 0.73.$$

$$\text{Molality} = \frac{\text{No. of solute moles}}{\text{wt. of solvent}} \times 1000.$$

$\because$ No. of moles of solute $= \frac{72}{98}$,

wt. of solvent = wt. of solution − wt. of solute

$$= (1000 \times 1.2) - 72 = 1128 \text{ g},$$

$$\therefore \quad \text{Molality} = \frac{72}{98 \times 1128} \times 1000 = 0.65.$$

16. Calculate the pH of 0.1 M solution of CH_3COOH if the degree of dissociation of acid is 0.0132.
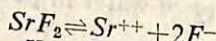
Solution : $\qquad CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Conc. of acid = 0.10 M

Degree of dissociation = 0.0132

$\therefore \ [H^+] = 0.1 \times 0.0132 = 0.00132$

$\therefore \ pH = -\log [H^+] = -\log [0.00132] = \log 13.2 + \log 10^{-4}$

$\qquad = 1.12057 - 4 = -2.87943.$

17. The solubility product value of SrF_2 at 298 K is 2.8×10^{-9}. Determine the solubility of SrF_2 at 298 K in moles per litre.

Solution :

$$SrF_2 \rightleftharpoons Sr^{++} + 2F^-$$
$$K_{sp} = [Sr^{++}] \times [F^-]^2$$

Let the solubility of SrF_2 be x moles per litre.

$\therefore \ [Sr^{++}] = x$ moles per litre

$[F^-] = 2x$ moles per litre.

$\therefore \quad x(2x)^2 = 2.8 \times 10^{-9}, \qquad$ or $\ 4x^3 = 2.8 \times 10^{-9}$

or $\qquad x^3 = 0.7 \times 10^{-9}, \qquad$ or $\qquad x = 8.9 \times 10^{-4}$ moles per litre.

18. The pH of a solution in which $[H^+] = 0.01$, is

(i) 2, $\quad$ (ii) 1, $\quad$ (iii) 4, $\quad$ (iv) 3, $\quad$ (v) 0.2.

(M. A. D. T. 1981)

Solution : $pH = -\log [H^+] = -\log 10^{-2} = 2.$

19. The pH of a solution obtained by adding 0.4 g solid $NaOH$ to 1.0 litre of water will be

(i) 8, $\quad$ (ii) 10, $\quad$ (iii) 11, $\quad$ (iv) 12.

(B. H. U. Medical Test 1981)

Solution : Conc. of $NaOH$ in solution $= 0\cdot4$ g per litre

$$= \frac{0\cdot4}{40}\text{ g}\quad\text{mole per litre} = 0\cdot01\text{ g mole per litre.}$$

i.e., $[OH^-] = 0\cdot01$ g mole per litre
$\qquad\qquad = 10^{-2}$ g mole per litre.

$\because\ [H^+]\times[OH^-] = 10^{-14}$, $\qquad\therefore\ [H^+]\times10^{-2} = 10^{-14}$

or $[H^+] = \dfrac{10^{-14}}{10^{-2}} = 10^{-12}$, $\quad\therefore\ pH = -\log 10^{-12} = 12.$

Hence, (iv) is correct.

20. Calculate the pH of 10^{-8} (N) HCl. (I. I. T. 1981)

Solution : $[H^+]$ from 10^{-8} (N) $HCl = 1 \cdot 0^8$
$\qquad\qquad [H^+]$ from $\qquad\qquad$ water $= 10^{-7}$
$\therefore$ Total $[H^+] = 10^{-8}+10^{-7} = 10^{-7}(10^{-1}+1) = 1\cdot1\times10^{-7}$
$\therefore\ pH = -\log[1\cdot1\times10^{-7}] = -[\log 1\cdot1 + \log 10^{-7}]$
or $pH = -[0\cdot0414-7] = 6\cdot0$.

21. 20 ml of $0\cdot2$ M $NaOH$ is added to 50 ml of $0\cdot2$ M acetic acid to give 70 ml of the solution. What is the pH of this solution ?

(I. I. T. 1982)

Solution : 20 ml $0\cdot2$ M $NaOH$ mixed with 50 ml $0\cdot2$ M CH_3COOH will produce 20 ml $0\cdot2$ M CH_3COONa.

Molarity of CH_3COONa in 70 ml solution :
$$20\times0\cdot2\text{ M} = 70\times x\text{ M}$$

$$\therefore\quad x = \frac{20\times0\cdot2}{70} = \frac{4}{70}.$$

$(50-20) = 30$ ml $0\cdot2$ M CH_3COOH is unneutralised.

Let the strength of CH_3COOH in 70 ml solution be 'a'. Then,

$$30\times0\cdot2\text{ M} = 70\times a\text{ M},\quad\text{or}\quad a = \frac{30\times0\cdot2}{70} = \frac{6}{70}.$$

Now, $pH = pK + \log\dfrac{[\text{salt}]}{[\text{acid}]} = -\log K + \log\dfrac{[\text{salt}]}{[\text{acid}]}$

$$= -\log(1\cdot8\times10^{-5}) + \log\frac{4/70}{6/70}$$

$$= -\log 1\cdot8 - \log 10^{-5} + \log 2/3$$

$$= -\log 1\cdot8 - \log 10^{-5} + \log 20 - \log 30$$

$$= -0\cdot2553 + 5 + 1\cdot3010 - 1\cdot4771 = 4\cdot5686 = 4\cdot57.$$

22. For the reaction, $A \rightarrow B+C$, the following data were obtained—

t in sec	0	900	1800
conc. of A	50·8	19·7	7·62

Prove that the reaction is of the first order.

Ans. From the question, initial conc. of A, i.e., $a = 50.8$.
At time 900 sec, $a - x = 19.7$.
The kinetic equation for the 1st order reaction is given by,

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{900} \log \frac{50.8}{19.7}$$

$$= \frac{2.303}{900} (\log 50.8 - \log 19.7)$$

$$= \frac{2.303}{900} (1.7059 - 1.2945)$$

$$= \frac{2.303}{900} \times 0.4114 = 1.05 \times 10^{-3}.$$

Now $\qquad k_2 = \frac{2.303}{1800} \log \frac{50.8}{7.62}$

$$= \frac{2.303}{1800} (\log 50.8 - \log 7.62)$$

$$= \frac{2.303}{1800} \times 0.8239 = 1.05 \times 10^{-3}$$

As the k value remains constant, the reaction is of the first order.

23. At 0°C the vapour pressure of water is 4.58 mm of Hg and that of the solution containing 8.8 g of solute per 100 g of water is 4.559 mm of Hg. Calculate the molecular weight of the substance.

Solution : Given : $P_0 = 4.58$, $P_s = 4.559$
$\qquad\qquad\qquad W = 100$, $w = 8.8$, $M = 18$, $m = ?$

According to Raoult's law of the lowering of vapour pressure,

$$\frac{P_0 - P_s}{P_0} = \frac{wM}{mW}$$

or $\quad \dfrac{4.58 \times 4.559}{4.58} = \dfrac{8.8 \times 18}{m \times 100}$, $\quad$ or $\quad \dfrac{0.021}{4.58} = \dfrac{8.8 \times 18}{m \times 100}$

or $\qquad\qquad m = \dfrac{8.8 \times 18 \times 4.58}{0.021 \times 100} = 345.4.$

24. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 27°C. If mole fraction of ethyl alcohol is

0·65, calculate its vapour pressure. The vapour pressure of propyl alcohol is 210 mm.

Solution : Mole fraction of ethyl alcohol $(n) = 0·65$

$\therefore$ Mole fraction of propyl alcohol $(N) = 1 - 0·65 = 0·35$

V. P. of mixture, $P = 290$ mm

$$p_N = 210 \text{ mm}, \qquad p_n = ?$$

Now $\qquad\qquad P = p_n \times n + p_N \times N$

or $\qquad\qquad 290 = p_n \times 0·65 + 210 \times 0·35$

or $\quad p_n = \dfrac{290 - (210 \times 0·35)}{0·65} = \dfrac{216·5}{0·65} = 333·1$ mm.

25. Freezing point of a biological fluid is $-0·55°C$. Calculate its osmotic pressure at $37°C$, assuming that the change in the temperature does not cause its solution characteristic. $K_f = 1·86°C$ per 1000 g of H_2O.

Solution : $\triangle T_f = 1000 \, K_f \cdot \dfrac{W_B}{M_B} \times \dfrac{1}{W_A}$.

W and M represent the molecular weights.

Here, $\qquad\qquad \triangle T_f = 0·55, \qquad K_f = 1·86$

$\therefore \qquad\qquad \dfrac{W_B}{M_B} = \dfrac{\triangle T_f}{1000 K_f} = \dfrac{0·56}{1000 \times 1·86}, \; (W_A = 1)$

or $\qquad\qquad \dfrac{W_B}{M_B} = 0·3013 \times 10^{-3} \text{ mole g}^{-1},$

$\therefore$ Mole of solute per 1000 g solvent, $(m) = 0·3013 \times 10^{-3} \times 10^3$
$$= 0·3013.$$

Now, Osmotic pressure, $\quad P = mRT$
$$= 0·3013 \times 0·082 \times 310 = 7·66 \text{ atm.}$$

26. In an electrolysis experiment, current was passed for 5 hours through two cells connected in series. The first cell contains a solution of gold and the second contains copper sulphate solution. 9·85 g of gold was deposited in the first cell. If the oxidation number of gold is $+3$, find the amount of copper deposited on the cathode of the second cell. Also, calculate the magnitude of the current in amperes. (1 Faraday = 96,500 coulombs) **(I. I. T. 1983)**

Solution : Wt. of gold deposited $= 9·85$ g

Atomic weight of gold $= 197$

O. N. of gold $= +3$

$\therefore$ Eq. wt. of gold $= \frac{197}{3}$.

Thus,

$\frac{197}{3}$ g Au will be deposited by 96,500 coulomb

$\therefore$ 9·85 g Au will be deposited by $\dfrac{96500 \times 9·85 \times 3}{197}$

$$= 14475 \text{ coulomb.}$$

Now, at wt. of $Cu = 63.5$

$$\text{O. N. of } Cu = +2, \quad \therefore \quad \text{Eq. wt. of } Cu = \frac{63.5}{2}.$$
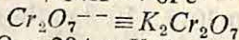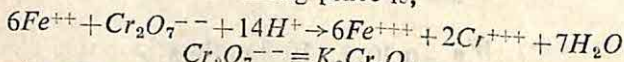
Thus,

96,500 coulomb will deposit $\frac{63.5}{2}$ g Cu,

$$\therefore \quad 14475 \text{ coulomb will deposit } \frac{63.5 \times 14475}{2 \times 96,500} \text{ g} = 4.76 \text{ g}$$

$$\text{Current required} = \frac{Q}{t} = \frac{14475}{5 \times 60 \times 60} = 0.804 \text{ A}.$$

27. 0.05 g sample of an iron containing mineral mainly in the form of $CuFeS_2$ was reduced suitably to convert all the ferric iron into the ferrous form and was obtained as solution In the absence of any interfering matter the solution required 42 ml of 0.001 M $K_2Cr_2O_7$ solution for the reaction. Calculate the percentage of $CuFeS_2$ in the mineral.

Solution : The reaction taking place is,
$$6Fe^{++} + Cr_2O_7^{--} + 14H^+ \rightarrow 6Fe^{+++} + 2Cr^{+++} + 7H_2O$$
$$Cr_2O_7^{--} \equiv K_2Cr_2O_7$$
1000 ml 1 M $K_2Cr_2O_7 = 294$ g $K_2Cr_2O_7$

42 ml 0.001 M $K_2Cr_2O_7 = \dfrac{294 \times 0.001 \times 42}{1000} = 0.012348$ g.

According to the equation above,
∵   294 g $K_2Cr_2O_7$ reacts with 6×55.8 g Fe,

∴   0.012348 g $K_2Cr_2O_7$ reacts with $\dfrac{6 \times 55.8 \times 0.012348}{294}$

$$= 0.14112 \text{ g } Fe.$$
∵ $CuFeS_2$ contains 1 atom of Fe,
∴   55.8 g of $Fe \equiv 183.3$ g $CuFeS_2$

∴   0.14112 g of $Fe \equiv \dfrac{183.3 \times 0.14112}{55.8}$ g $CuFeS_2 = 0.46357$ g

Wt. of the sample $= 0.5$ g

∴   100 g of the sample contains $\dfrac{0.46357 \times 100}{0.5}$ g

$$= 92.72 \text{ g } CuFeS_2.$$

28. What is the composition by volume of a mixture of

methane, ethylene and acetylene which gave the following results ?

18·4 ml of the mixed gases was added to 100 ml of oxygen and exploded. The contraction after the explosion was found to be 33·2 ml. Treatment of the residual gases with potash decreased the volume by 31·4 ml. (All volumes are measured at S. T. P.).

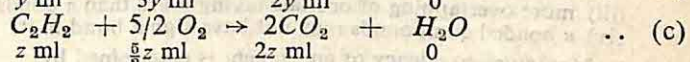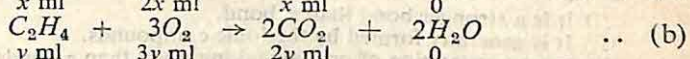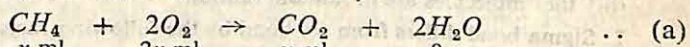**Solution** : Let the volume of methane $= x$ ml
$$\text{Volume of ethylene} = y \text{ ml}$$
$$\text{Volume of acetylene} = z \text{ ml}$$
$$\therefore \quad x + y + z = 18\cdot4 \qquad \qquad \text{.. (i)}$$

The equations for the reactions will be,

$$\underset{\underset{x \text{ ml}}{}}{CH_4} + \underset{\underset{2x \text{ ml}}{}}{2O_2} \rightarrow \underset{\underset{x \text{ ml}}{}}{CO_2} + \underset{\underset{0}{}}{2H_2O} \qquad \text{.. (a)}$$

$$\underset{\underset{y \text{ ml}}{}}{C_2H_4} + \underset{\underset{3y \text{ ml}}{}}{3O_2} \rightarrow \underset{\underset{2y \text{ ml}}{}}{2CO_2} + \underset{\underset{0}{}}{2H_2O} \qquad \text{.. (b)}$$

$$\underset{\underset{z \text{ ml}}{}}{C_2H_2} + \underset{\underset{\frac{5}{2}z \text{ ml}}{}}{5/2\,O_2} \rightarrow \underset{\underset{2z \text{ ml}}{}}{2CO_2} + \underset{\underset{0}{}}{H_2O} \qquad \text{.. (c)}$$

Amount of O_2 left = (Volume of gases before explosion)
  − (contraction on explosion and on treatment with KOH)
$$= (100 + 18\cdot4) - (33\cdot2 - 31\cdot4) = 53\cdot8 \text{ ml}$$
$\therefore$ Volume of O_2 used in reaction $= 100 - 53\cdot8 = 46\cdot2$ ml
Volume of O_2 used $= 2x + 3y + \frac{5}{2}z$
$$\therefore \quad 2x + 3y + \tfrac{5}{2}z = 46\cdot2 \qquad \text{.. (ii)}$$
Volume of $CO_2 = x + 2y + 2z$
$$\therefore \quad x + 2y + 2z = 31\cdot4 \qquad \text{.. (iii)}$$

Multiply (i) by 2 and subtract the result from (iii),
$$x + 2y + 2z = 31\cdot4$$
$$2x + 2y + 2z = 36\cdot8$$
$$\overline{}$$
$$-x = -5\cdot4$$
$$\text{or} \qquad x = 5\cdot4 \text{ ml}$$

Adding (iii) and (i) and subtracting (ii) :
$$2x + 3y + 3z - 2x - 3y - \tfrac{5}{2}z = 18\cdot4 + 31\cdot4 - 46\cdot2$$
or $\qquad \frac{1}{2}z = 3\cdot6, \qquad \therefore \quad z = 7\cdot2$ ml
Now, $\qquad x + y + z = 18\cdot4, \qquad \therefore \quad 5\cdot4 + y + 7\cdot2 = 18\cdot4$
or $\qquad 12\cdot6 + y = 18\cdot4, \qquad \therefore \quad y = 18\cdot4 - 12\cdot6 = 5\cdot8$ ml.

Multiple Choice Questions :

1. The element used to kill bacteria in drinking water is
(i) Ca (ii) Cl (iii) Mg (iv) none of the above.

2. The accurate value of absolute zero is
(i) 273°C (ii) —273°C (iii) 273·15°C (iv) —273·15°C.

3. The formation of a chemical bond is associated with
(i) a decrease in potential energy (ii) an increase in potential energy (iii) decrease in volume (iv) increase in volume.

4. The critical temperature of a gas is the temperature at which
(i) the gas is liquified
(ii) the kinetic energy of gas molecules is highest

(iii) gas can be liquified just by increasing the pressure only
(iv) none of the above.

5. Which one of the following factors determines whether a substance has metallic properties or not ?

(i) atomic number
(ii) atomic mass
(iii) number of valence electrons
(iv) total number of electronic shells in the atom.

6. The halogen molecules are coloured because

(i) it is their characteristic property
(ii) their molecules absorb some of the frequencies of visible light
(iii) the molecules are in random motion.

7. Sigma bond differs from pie bond by the following facts except

(i) it is a stronger bond than π bond.
(ii) it is generally formed by the ionic compounds.
(iii) more overlapping of orbitals taking place than π bonds.
(iv) π bonded compounds may not have sigma bond in it.

8. Maximum covalency of an element is determined by

(i) the number of valence electrons in an atom.
(ii) the number of covalent bonds which that element can form.
(iii) maximum possible valency of the element.
(iv) maximum number of isotopes an element can form.

9. The inert pair effect in heavier elements is due to the reluctance of the pair electrons

(i) s-orbital (ii) p-orbital (iii) d-orbital (iv) f-orbital.

10. Which one of the following has octahedral shape ?

(i) CH_4 (ii) PCl_5 (iii) SF_6 (iv) IF_7.

11. A compound contains atoms of A, B and C. The oxidation number of A is $+2$, of B is $+5$ and of C is -2. A possible molecular form when these atoms combine is

(i) ABC_2 (ii) $A_2(BC_3)_2$ (iii) $A_3(BC_4)_2$ (iv) $A_3(B_4C)_2$.

12. Which one of the following would have an unpaired electrons ?

(i) SO_2 (ii) NO_2^- (iii) NO_2^+ (iv) NO_2.

13. Dewar method is used for the separation of

(i) Halogens (ii) Noble gases (iii) Lanthanides (iv) Actinides.

14. Phosphorus exposed to the atmosphere burns spontaneously because

(i) the activation energy of phosphorus is very low
(ii) air catalyses the reaction.
(iii) burning of phosphorus is exothermic.
(iv) none of these.

15. The characteristic half life of an unstable isotope is strongly influenced by

(i) temperature
(iii) either of these
(ii) pressure
(iv) neither of these.

16. If the standard free energy change is negative in sign, the reaction

(i) will take place spontaneously.
(ii) will be exothermic
(iii) will be endothermic
(iv) will not occur.

17. Radioactive isotopes that have an excessive neutron-proton ratio generally exhibit

(i) α-emission
(iii) β-emission
(ii) positron emission
(iv) κ-capture.

18. The phenomenon of ejection of electrons from a metal surface by the action of light is called

    (i) Compton effect   (ii) Photoelectric effect
    (iii) Zeeman effect   (iv) None of these.

19. What is the atomic number of the element which has maximum number of unpaired $3p$ electrons ?

    (i) 15   (ii) 26   (iii) 23   (iv) 33.

20. Which one of the following materials is used for Control rods in uranium reactors ?

    (i) Antimony   (ii) Boron steel   (iii) Carbon steel   (iv) Titanium.

Ans. 1. (ii); 2. (iv); 3. (i); 4. (iii); 5. (iii); 6. (ii); 7. (iv); 8. (ii); 9. (iii); 10. (iii); 11. (iii); 12. (iv); 13. (ii); 14. (i); 15. (iv); 16. (i); 17. (iii); 18. (ii); 19. (i); 20. (ii).

□ □ □

APPENDIX I

Some Physical Constants

Avogadro's number $(N) = 6 \cdot 023 \times 10^{23}$
Planck constant $(h) = 6 \cdot 624 \times 10^{-27}$ erg-sec
Velocity of light $(c) = 3 \times 10^{10}$ cm per sec.
Electronic charge $(e) = 4 \cdot 8022 \times 10^{-10}$ e. s. u.
$\qquad = 1 \cdot 602 \times 10^{-19}$ coulomb
Electronic mass $(m_e) = 9 \cdot 1072 \times 10^{-28}$ g
Proton mass $(m_p) = 1 \cdot 6722 \times 10^{-23}$ g
Neutron mass $(m_n) = 1 \cdot 6750 \times 10^{-24}$ g
1 Angstrom $(A^\circ) = 10^{-8}$ cm
1 litre (1000 ml) $= 1000 \cdot 027$ c.c.
1 atmosphere $= 76$ cm of Hg
$\qquad = 76 \times 13 \cdot 6 \times 981$ dyne cm^2
Absolute Zero of temperature $= -273 \cdot 15°C$
1 calorie $= 4 \cdot 185$ joules
1 joule $= 0 \cdot 2389$ calorie
Gas constant $(R) = 8 \cdot 314 \times 10^7$ erg^{-1} deg mol^{-1}
$\qquad = 0 \cdot 0821$ litre-atm deg^{-1} mol^{-1}
$\qquad = 1 \cdot 987$ calorie
$\qquad \approx 2$ calorie deg^{-1} mol^{-1}
Faraday $(F) = 96496$ coulomb per gram
$\qquad\qquad$ equivalent
$\qquad \approx 96500$ coulomb per gram
$\qquad\qquad$ equivalent.

APPENDIX II

International System of Units (S I)

A

S I Base Units

Quantity	Name of Unit	Symbol
Length	Metre	m
Mass	Kliogram	kg
Time	Second	s
Electric current	Ampere	A
Temperature	Kelvin	K
Amount	Mole	mol

B

S I Derived Units

Quantity	Name of Unit	Symbol
Volume	Cubic metre	m³
Volume	Liter	l
Pressure	Pascal	Pa
Energy	Joule	J
Energy	Calorie	cal
Electric charge	Coulomb	C
Electric potential	Volt	V
Electric resistance	Ohm	Ω
Length	Angstrom	Å

C

Some Physical constants

Velocity of light	c	$2 \cdot 997925 \times 10^8$ m sec^{-1}
Avogadro's number	N	$6 \cdot 0225 \times 10^{23}$ particles mole^{-1}
Planck's constant	h	$6 \cdot 6256 \times 10^{-24}$ joule sec^{-1}
		$6 \cdot 6256 \times 10^{-27}$ erg sec
Gas constant	R	$0 \cdot 082054$ liter atm deg^{-1} mole^{-1}
		$8 \cdot 3143$ joules deg^{-1} mole^{-1}
		$1 \cdot 9872$ cal deg^{-1} mole^{-1}
Atomic mass unit		$1 \cdot 66053 \times 10^{-27}$ kg
Electron charge	e	$1 \cdot 60219 \times 10^{-9}$ coulomb
		$4 \cdot 80298 \times 10^{-10}$ e. s. u.
Electron radius		$2 \cdot 8177 \times 10^{-15}$ m
		$2 \cdot 8177 \times 10^{-12}$ cm

APPENDIX III

Conversion Factors

1 erg	=	1×10^{-7} joule
1 coulomb	=	$6 \cdot 281 \times 10^{18}$ electronic charges
1 electron volt	=	$1 \cdot 602 \times 10^{-12}$ erg
	=	$1 \cdot 602 \times 10^{-19}$ joule
	=	$3 \cdot 287 \times 10^{-20}$ cal
1 Faraday	=	$96 \cdot 487$ coulombs mole^{-1}
1 metre	=	$39 \cdot 37$ inches
1 kilogram	=	$2 \cdot 205$ pounds
1 atmosphere	=	760 torr
	=	$1 \cdot 013 \times 10^6$ dynes cm^{-2}
	=	101,325 newtons metre^{-2}

APPENDIX IV

Vapour Pressure of Water

t°C	Torr	t°C	Torr
0	4·58	25	23·76
5	6·54	30	31·82
10	9·21	35	42·18
15	12·79	40	55·32
20	17·54	45	71·88

□ □ □

541